

*V.Z. Bugakov*

**Diffusion  
in  
Metals  
and  
Alloys**







*PROBLEMS OF MODERN PHYSICS*

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# DIFFUSION IN METALS AND ALLOYS

(Diffuziya v metallakh i splavakh)

Gosudarstvennoe Izdatel'stvo  
Tekhniko-Teoreticheskoi Literatury

Leningrad — Moskva  
1949

Translated from Russian

Israel Program for Scientific Translations  
Jerusalem 1971

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Israel Program for Scientific Translations Ltd.  
IPST Cat. No. 5678

Translated by Ch. Nisenbaum, Chem. Eng.  
Edited by D. Slutzkin

Printed in Jerusalem by Keter Press  
Binding: Wiener Bindery Ltd., Jerusalem

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## FOREWORD

This monograph on "Diffusion in Metals and Alloys" is a brief review of studies on the most important and general problems of the diffusion of metals carried out by V. Z. Bugakov and co-workers.

Although the works of both Soviet and non-Soviet authors are included, the book is based on V. Z. Bugakov's dissertation for the degree of doctor.

There are two parts.

Part I. Atomic Diffusion of Metals;

Part II. Reactive Diffusion of Metals.

The first and second chapters of Part II were written by V. Z. Bugakov and D. Ya. Gluskin.

This book is of great theoretical and practical interest to physicists, metallurgists, and advanced students.

The life of V. Z. Bugakov, who was a young and gifted scientist, was cut short by the Nazi invasion and the siege of Leningrad.

D. Gluskin



## INTRODUCTION

Diffusion is one of the most important problems of metallurgy, as it influences the melting and solidification of metals and alloys, hot working and heat treatment, plastic deformation and recrystallization, etc.

Diffusion greatly affects the increasingly important processes of diffusion coating of metals and alloys.

The founders of metallurgy, Chernov, Osmond, Le Chatelier, Roberts-Austen, and others took great interest in diffusion. This interest increased during the following years, but the study of diffusion on the basis of physical theories of the thermal motion of atoms in liquids and in solids started only in the twenties, and since then these studies have ceased to be purely empirical. By measuring the constants which correlate the motion of atoms to their state in the crystal lattice, it is possible to compare the results of experiments, and assess modern theories of diffusion which involve problems that must be solved experimentally. Today, we can attempt to determine certain relationships between the mobility of atoms in metals and the nature and structure of these metals, and thus solve more general problems.

This monograph describes the study of some general problems on metal diffusion, and is divided into two parts. The first part deals with problems of the motion of atoms in a single phase ("atomic diffusion"), which leads to the formation of solid solutions with a lattice of the solvent metal. It also discusses the temperature dependence of the diffusion coefficient, the influence of structural factors on the diffusion rate, and the dependence of the diffusion coefficient on the concentration of the diffusing metal.

We believe that these problems are most important, as they largely determine the processes of diffusion in metals.

The temperature dependence of the diffusion coefficient, which relates the mobility of the atoms to their position in the crystal lattice, is the fundamental problem of diffusion. Therefore, the study of the most important factors which determine the temperature dependence of the diffusion coefficient is of great practical and theoretical interest. We investigated this temperature dependence by making a detailed analysis of the available data on metal diffusion.

The role of the structure of metals in the process of diffusion is not less important. Although the influence of structure is undeniable, the degree and nature of this influence have not yet been sufficiently studied. In this paper we discuss these on the basis of the results of our own investigations.

The last chapter of Part One (on the dependence of the diffusion coefficient on concentration) discusses the applicability of the classic laws of diffusion of metals.

Part Two of this book describes studies on the reactive diffusion in metals which leads to the formation of new phases with structures different from those of the diffusing metals.

We investigated the most important problems of reactive diffusion and the nature, formation, and growth of the phases produced during this process.

Great attention was paid to the little studied reactions between heat-resistant metals and liquid low-melting metals. These reactions occur in many processes of metal coating, and are therefore of great practical interest.

In the last chapter of the book we shall discuss the kinetics of the reactions between solid and liquid metals taking as an example zinc coating on iron.

The main problems in the study of reactive diffusion were therefore to clarify the many factors determining the structure of diffusion layers, to find the laws governing their growth, and to develop methods for studying the kinetics of technical processes involving the reaction between a heat-resistant metal and a liquid low-melting metal.

## *Part One*

### *ATOMIC DIFFUSION OF METALS*

#### *Chapter I*

#### *MOBILITY OF ATOMS IN THE CRYSTAL LATTICE OF METALS*

##### **§ 1. Atomic diffusion**

Diffusion limited to the motion of the atoms of one metal in the lattice of another metal is called atomic diffusion. This type of diffusion can be fairly easily interpreted physically, and therefore it has been most widely studied. This diffusion leads to the formation of only solid solutions with a lattice of the solvent metal. No new phases with a structure different from that of the solvent metal can be formed. Hence, it follows that the maximum concentration of the diffusing metal in the solvent metal cannot exceed the maximum concentration in a solid solution formed at a given temperature.

The quantitative evaluation of atomic diffusion is determined by the diffusion coefficients, which characterizes the rate of this process. The diffusion process is studied to find ways for quantitatively calculating the diffusion coefficients and their temperature dependence. The starting point for these studies is the determination of the mechanism of the motion of atoms in crystal lattices.

The simplest case is the motion of atoms of a pure metal in its own crystal lattice.

This case, called self-diffusion, is the starting point for all modern theoretical studies on the problem of the diffusion of metals.

##### **§ 2. Self-diffusion of metals**

The assumption that the motion of atoms of a solid crystal is limited to oscillation about their equilibrium position cannot explain a number of known phenomena, including diffusion of metals and the electrolytic conductivity of salts. Today, we differentiate between two types of atomic motion: 1) oscillation about the equilibrium configuration; and 2) motion of atoms from one equilibrium configuration to another. This means that the equilibrium configuration should be considered as metastable. It is clear that these ideas should be related not only to impurity atoms which penetrate the lattice of another metal, but also to the atoms of the same metal, irrespective of whether or not it contains foreign atoms. In the last case we have self-diffusion.

Long before these theories were established, in 1877, Chernov /1/ found that two pieces of the same metal (iron), with a good contact, become welded when heated to 650°C. Later, in 1899, examples of self-diffusion were given by Austen /2/. At that time it was difficult to give quantitative experimental proof of this phenomenon, because it was impossible to label atoms of the same metal and follow their motion in the crystal lattice. This obstacle was overcome in 1920 by Hevesy /3/ and co-workers.

To determine the coefficient of self-diffusion, they used radioactive isotopes of lead. The radioactive atoms can be differentiated from the stable atoms of lead. In the method using radioactive atoms the surface of a plate of nonradioactive lead (or lead salts, for example,  $\text{PbI}_2$ ,  $\text{PbCl}_2$ , etc.) was covered by a radioactive isotope of lead (for example,  $\text{ThB}$ ), and the intensity of the radiation was determined by counting the number of scintillations on a screen coated with a fluorescent substance, or by measuring the degree of ionization of air.

As the diffusion of the radioactive atoms of lead from the surface into the interior of the lead plate increases, the number of scintillations and the degree of ionization of air decrease. This decrease determines the rate at which the radioactive atom of lead penetrates by diffusion into the non-radioactive lead. The coefficient of self-diffusion was calculated from the length of the free path of a  $\beta$ -particle in lead, equal to approximately 1/30 mm, or from the length of the free path of Ra-B particles, about  $3 \cdot 10^{-5}$  mm.

The values of the diffusion coefficients determined by the radioactive method were accurate to within  $10^{-13}$   $\text{cm}^2/\text{sec}$ . By this method the authors measured the coefficients of self-diffusion of lead at various temperatures.

According to their data, the coefficient of self-diffusion of lead is appreciably smaller than the diffusion coefficients of other metals in lead.

It was found that the temperature dependence of the coefficient of self-diffusion of lead is governed by an exponential law, and this was later reconfirmed. The temperature dependence can be written:

$$D = 5.76 \cdot 10^6 e^{-\frac{14025}{T}} \text{ cm}^2/\text{day},$$

where  $D$  is the coefficient of self-diffusion of lead at temperature  $T$  (absolute temperature), and  $e$  is the base of natural logarithms.

In a general form the equation can be written:

$$D = Ae^{-Q/RT}. \quad (1)$$

As we shall see later, equation (1) holds not only for self-diffusion, but also for all types of diffusion of one metal in another that have so far been investigated. This equation and its constants are analogous to those derived for the rate of unimolecular reactions. The coefficient  $A$  is usually called the "temperature dependent factor,"\* and it is formally equal to the coefficient of diffusion at a temperature equal to infinity. The coefficient  $Q$  is the most important characteristic of the process, called the heat of "loosening" in analogy to the heat of activation in the theory of chemical reactions.

The value  $Q$  is related to the theory of loosening of the crystal lattice due to weakening of the interatomic bonds and to increase in the possible migration of atoms from their equilibrium position.

\* As we shall see later this is not quite accurate.

Equation (1) shows that the heat of "loosening" can be experimentally determined from the slope of the curve plotted in  $\ln D$  and  $1/T$  coordinates.

The papers of Hevesy and co-workers on the self-diffusion of lead were followed by a number of theoretical studies on the mobility of atoms in crystal lattices.

However, the development of the theory of diffusion was greatly hampered by lack of experimental data, especially in the field of self-diffusion. A comparison between the coefficients of self-diffusion and the parameters of their temperature dependence (particularly the value of  $Q$ ) for various metals would be of great importance for theoretical research. But until artificial radioactivity was discovered, the only metal with a radioactive isotope which could be used as a tracer for studying self-diffusion was lead.

After artificial radioactivity had been discovered, it became possible to obtain radioactive isotopes of many metals by bombarding them with heavy particles (neutrons, protons, deuterons). Soon after their discovery these radioactive isotopes were widely used as tracers in various fields of physics, chemistry, physical chemistry, biology and other sciences. Attempts were also made to use them for determining the coefficients of self-diffusion of metals.

One of the first studies in the field was carried out by Zagrubskii /4/ of the Laboratory of Diffusion of the Ural Physical Technical Institute. He measured the coefficient of self-diffusion of gold at various temperatures.

Gold was used because experiments on diffusion, even at elevated temperatures, take a long time, and therefore an element must be chosen with a high activity and a long half-life. Radioactive gold, which has a half-life of 65 hours, is suitable.

Zagrubskii obtained radioactive gold by irradiating a gold plate for 10–12 hours in a paraffin vessel containing an emanation and beryllium powder. The plate of radioactive gold was electrolytically coated by a layer of ordinary gold about 0.01 mm thick. The plate was then placed in a furnace and held for a given time at constant temperature. As a result of self-diffusion the electrolytic gold was penetrated by radioactive atoms. The number of atoms was found by measuring the  $\beta$ -radiation in separate layers which were electrolytically removed in succession.

The activity was measured by a Geiger counter. When the concentration of radioactive atoms at different distances from the boundary layer was known, it was possible to calculate the coefficient of self-diffusion of radioactive gold in ordinary gold.

Zagrubskii carried out measurements at different temperatures, and found the temperature dependence of the coefficient of self-diffusion of gold. Like the temperature dependence of self-diffusion of lead, this is governed by an exponential law, and can be written as follows:

$$D = 1.36 \cdot 10^4 e^{-\frac{53000}{RT}},$$

i. e., the coefficient  $A$  is equal to  $1.36 \cdot 10^4$ , and the heat of loosening is  $Q = 53,000$  cal/mole.

The self-diffusion of gold was also studied by McKay /5/, who used a method similar to that of Zagrubskii, and found the following temperature

dependence of the coefficient of self-diffusion:

$$D = 0.87 \cdot 10^3 e^{-\frac{51000}{RT}},$$

i. e.

$$A = 0.87 \cdot 10^3 \text{ cm}^2/\text{day},$$

and

$$Q = 51,000 \text{ cal/mole}.$$

These results differ little from those of Zagrubskii.

The self-diffusion of copper has recently been studied also. As a tracer Rollin /6/ used the radioactive  $\text{Cu}_{29}^{64}$  copper isotope, which he obtained by bombardment with deuterons.

The distribution of the activity after diffusion was measured by removing individual layers and measuring their activity by an electrometer.

Rollin /6/ found the coefficient of self-diffusion at three temperatures, and calculated the heat of loosening:

$$Q = 61,400 \text{ cal/mole}.$$

The self-diffusion of copper was also measured by Steigman, Shockley, and Nic /7/ who used radioactive copper as tracer, obtained by bombarding zinc with neutrons. The distribution of radioactive copper after diffusion was found from the change in the flux of  $\beta$ -particles. As the coefficient of absorption of  $\beta$ -particles by copper was known, the coefficient of self-diffusion could be calculated from:

$$Q = 57,200 \text{ cal/mole},$$

$$A = 11 \text{ cm}^2/\text{sec}.$$

These results differ somewhat from those of Rollin.

### §3. Principal factors in the development of the statistical theory of diffusion

As we have already mentioned, diffusion in solids and electrolytic conductivity in solid dielectrics indicate that the motion of atoms in crystal lattices is not limited to oscillation about their equilibrium configuration, and a new theory on the motion of atoms in solids was therefore developed. The experiments of Hevesy on the self-diffusion of lead confirmed the translational motion of atoms of solids and formed the first experimental basis for the theoretical development of this problem.

The first and simplest model of the motion of atoms was given by Hevesy, who believed that this motion is the result of an interchange in the positions of atoms.

Braunne /8/ attempted to derive a quantitative theory of thermal motion from simple statistical considerations. He assumed that every atom of a salt can interchange places with neighboring atoms if the amplitudes of its oscillations exceed a certain mean value  $r_0$ . Atoms with an amplitude  $r < r_0$



are not able to interchange places, but only atoms with an amplitude  $r > r_0$ . The number of such atoms can be found from the equation:

$$\frac{dN}{N} = e^{-\frac{E}{kT}},$$

where  $E$  is the energy of atoms with an amplitude of oscillation  $r_0$ , and  $N$  is the number of atoms per  $\text{cm}^3$ . Hence, the number of atoms which can interchange with other atoms per unit time, and therefore the coefficient of diffusion, can be found from the equation:

$$D = Ce^{-\frac{E}{kT}}. \quad (1)$$

Later, Braunne attempted to derive an equation to find the energy  $E$ . He neglected the asymmetry of oscillations, and derived the following equation for this energy:

$$E = a^2 r_0^2$$

and

$$D = Ce^{-\frac{a^2 r_0^2}{kT}}.$$

Braunne related the value  $r_0$  to the value  $r_s$ , the mean amplitude of atoms during the melting of solids, by assuming that  $r_0 = br_s$ , where  $b$  is a number close to unity.

Braunne's formula draws an analogy between diffusion and melting and stresses the direct relationship between these phenomena. This agrees with Lindemann's theory that melting starts when the mean amplitude reaches a certain value directly related to the distance between the centers of gravity of atoms.

The potential energy of an atom at the melting point is equal to  $a^2 r_s^2$ , and also to  $3kT_s$ , where  $T_s$  is the melting point, and hence:

$$a^2 = \frac{3kT_s}{r_s^2} = \frac{3b^2 kT_s}{r_0^2},$$

The coefficient of diffusion at temperature  $T$  is equal to:

$$D_T = Ce^{-\frac{3b^2 kT_s}{T}}. \quad (2)$$

By comparing equation (1) with equation (2) we obtain:

$$\frac{Q}{R} = 3b^2 T_s, \quad (3)$$

and thus the Braunne theory indicates that the heat of loosening is proportional to the melting point.

The assumption of Hevesy (taken by Braunne as the basis of his theory) that diffusion is caused by direct interchange of pairs of neighboring atoms is not completely correct. Thus, it excludes possible individual movement of an atom, irrespective of the movement of its neighbors.

It is also clear that the probability of the simultaneous migration of two neighboring atoms is very slight, and also, the electrical conductivity of ionic crystals cannot be explained simply by the rearrangement of atoms.\* As a result, it has been assumed that other types of motion of atoms in the crystal lattice are also possible.

The idea of such types of motion was first introduced by Joffe, and became the basis for the quantitative theory of diffusion developed by Frenkel /9/.

According to Frenkel the thermal motion of atoms consists of the following processes:

1. Oscillation of atoms about a regular equilibrium configuration;
2. An atom (or an ion) with a sufficiently high energy can be shifted from its normal position in the lattice site into an "irregular" position, that is into an interstice. Frenkel calls this process "dissociation" of bound atoms. The probability of dissociation of atoms or of ions, or the probability of a transition in unit time from the regular position into an irregular one is designated by  $\alpha$ .

3. A dissociated atom can oscillate for a long time about its regular position before it jumps over the potential barrier into another free (regular or irregular) site.

4. An ion can jump from its irregular position into another irregular position over a distance  $\delta$ . The probability of this happening is designated by  $\alpha'$ .

5. A dissociated atom can also migrate (probability  $\beta$ ) into a vacant lattice site (vacancy).

This process Frenkel calls "association" of dissociated atoms.

6. And finally, a rearrangement of vacancies is possible, since in a state of thermal equilibrium a certain number of atoms occupy interstitial positions, and therefore there is a corresponding number of vacancies in the crystal lattice. The probability that an atom (ion) jumps over the potential barrier from a regular position into another regular position is designated by  $\alpha''$ .

Frenkel called the process of atoms jumping from one regular equilibrium position into another the diffusion of vacancies in the lattice. Both processes, the rearrangement of vacancies and the motion of atoms in the interatomic space, that is the motion of dissociated atoms, produce a diffusion and electrolytic conductivity of crystals. The probability of collision between a vacancy and a migrating dissociated atom during one second is proportional to  $n'$  and  $n''$  that is:

$$\beta = \gamma n' n'', \quad (1')$$

where  $n'$  is the number of vacancies;  $n''$  is the number of dissociated atoms per unit volume; and  $\gamma$  is the proportionality factor.

If the dissociated atoms are uniformly distributed in the crystal, then:  $n' = n''$  and  $\beta = \gamma n'^2$ . If we assume that in the general case the variation in the number of dissociated atoms with time  $\frac{dn'}{dt}$  can be represented by the formula:

$$\frac{dn'}{dt} = \alpha(n_0 - n') - \gamma n'^2, \quad (2')$$

\* Since such a rearrangement cannot produce a current in ionic crystals.

where  $n_0$  is the total number of atoms per unit volume;  $(n_0 - n')$  is the number of undissociated atoms; then for a stationary state we have:

$$\text{hence:} \quad \gamma n'^2 + \alpha n' - \alpha n_0 = 0,$$

$$n' = \frac{-\alpha + \sqrt{\alpha^2 + 4\gamma\alpha n_0}}{2\gamma}. \quad (3')$$

At ordinary temperatures and pressures the number of dissociated atoms is small compared to the total number of atoms per unit volume, and thus the following approximate formula can be written:

$$\frac{n'}{n_0} \approx \sqrt{\frac{\alpha}{\gamma n_0}}. \quad (3'')$$

Frenkel also believes that in analogy with the formula which he derived for molecules evaporating from the surface of a solid substance, the values of  $\alpha$ ,  $\alpha'$  and  $\alpha''$  are related to temperature by the exponential law:

$$\frac{1}{\alpha} = \tau = \tau_0 e^{\frac{u_0}{kT}},$$

$\tau$  is the mean time of residence of an atom (ion) in a regular equilibrium position;  $\tau_0$  is the period of its free (thermal) oscillation; and  $u_0$  is the work needed to remove an atom from a "regular" equilibrium position to an irregular position, that is into an interstice.

A similar formula can be written for  $\alpha'$  and  $\alpha''$ :

$$\frac{1}{\alpha'} = \tau' = \tau'_0 e^{\frac{u'_0}{kT}}; \quad \frac{1}{\alpha''} = \tau'' = \tau''_0 e^{\frac{u''_0}{kT}}.$$

To assess the factor  $\gamma$  it is assumed that  $\rho$  is the effective diameter of atoms and that the association of atoms takes place only if the distance from the dissociated atom to the vacancy is  $\leq \rho$ . Let the dissociated atom migrating within the lattice move along a path  $\bar{L}$  before it collides with a vacancy. It is obvious that the effective cross section of the atom is equal to  $\pi\rho^2$ , and the volume to  $\pi\rho^2\bar{L}$ . Then, the mean length  $\bar{L}$ , the path of the atom before collision with the vacancy, will be determined (in analogy to the mean path in the kinetic theory of gases) by:

$$n''\pi\rho^2\bar{L} = 1.$$

This mean path  $\bar{L}$  is traveled by the dissociated atom. The atom jumps successively through a distance  $\delta$ , which is the distance between two irregular positions and equal approximately to the distance between two neighboring normal (nondissociated) atoms in the crystal lattice. The mean rate  $\bar{v}$  of the motion of the dissociated atom within the lattice is equal to:

$$\bar{v} = \frac{\delta}{\tau} = \frac{\delta}{\tau_0} e^{-\frac{u_0}{kT}},$$

since it can be assumed that the time for traveling the path  $\delta$  usually coincides with  $\tau'$ . Consequently, the time for traveling the mean path  $\bar{L}$  will be  $t = \frac{\bar{L}}{v} = \frac{\tau'}{n'' \pi \rho^2 \delta}$ . If we divide the number of dissociated atoms  $n'$  by  $t$ , we obtain the number of atoms per unit time per unit volume, that is:

$$\frac{n'}{t} = \frac{n' n'' \pi \rho^2 \delta}{\tau'} = \beta = \gamma n' n'',$$

hence:

$$\gamma = \frac{\pi \rho^2 \delta}{\tau'}.$$

Since  $\pi \rho^2 \delta$  is of the order of magnitude of the volume, we can assume that approximately:

$$\pi \rho^2 \delta = \frac{q}{n_0}, \quad \text{where} \quad q \cong 1.$$

Equation (3') can be written as:

$$\frac{n'}{n_0} = \sqrt{\frac{\alpha \tau' n_0}{n_0 q}} = \sqrt{\frac{\tau'}{q \tau}}, \quad (4)$$

$$\text{i. e.} \quad \frac{n'}{n_0} = \sqrt{\frac{\tau_0}{q \tau_0}} e^{\frac{-u_0 + u'_0}{2kT}}.$$

In analogy with the theory of the Brownian motion described by Einstein, the coefficient of diffusion  $D'$  of dissociated atoms is equal to  $D = \frac{1}{6} \frac{\delta^2}{\tau'}$ . On the other hand, we can assume, like Hevesy, that all  $n_0$  atoms can participate in the interchange of positions, since the final result of this is the same. If we designate the coefficient of self-diffusion by  $D$ , we obtain:

$$D n_0 = D' n' \quad \text{or} \quad D = D' \frac{n'}{n_0} = \frac{\delta^2}{6 \tau'} \frac{n'}{n_0},$$

i. e.

$$D = \frac{\delta^2}{6 \sqrt{q \tau_0 \tau_0}} \cdot e^{\frac{-u_0 + u'_0}{2kT}}. \quad (5)$$

If we assume

$$\frac{u_0 + u'_0}{2} = u \quad \text{and} \quad \sqrt{q \tau_0 \tau_0} = \tau_0,$$

we obtain:

$$D = \frac{\delta}{6 \tau_0} e^{-\frac{u}{kT}}. \quad (5')$$

Formula (5') was derived by Frenkel, and correctly describes the general course of the experimentally found temperature dependence of the coefficient of self-diffusion. If we take this dependence in the general form:

$$D = A e^{-Q/RT},$$

then according to Frenkel we assume that the coefficient  $A$  is equal to:

$$A = \frac{\delta^2}{\delta \tau_0}. \quad (6)$$

The value  $A$  can easily be calculated from formula (6), since  $\delta$ , the distance between neighboring atoms in the lattice, and  $\tau_0$ , the period of natural oscillation of the atom (equal to approximately  $1/\nu$ , where  $\nu$  is the maximum frequency of oscillation), are known for almost all metals.

The Frenkel theory does not mention the fundamental magnitude which determines the mobility of atoms in the lattice (heat of loosening), which means that from the theory it is not possible to calculate this heat from any specific parameters of the solid, and the dependence of this magnitude on other physical properties is not indicated.

To correlate the value  $Q$  with other properties of solids and thus make it possible to calculate  $Q$ , it is apparently necessary to find more specific correlations between various types of rearrangements of atoms in the lattice, and in particular to solve the question as to which of these types, (interchange of positions; rearrangement within the lattice; or vacancy migration) is the dominating factor determining the rate of diffusion.

The Frenkel theory appeared at the beginning of the systematic study of diffusion of metals, and at the time when data on self-diffusion were available for lead only (those obtained by Hevesy). This hampered further development of the theories first proposed by Frenkel. Only recently after certain experimental data on the diffusion of metals have been accumulated, and the coefficient of self-diffusion of two other metals (gold and copper) have been obtained, new attempts have been made to further develop the theory of diffusion in the general direction shown by Frenkel.

One of these attempts was recently made by Johnson /10/. His work was based on the fact, proved experimentally, that the heat of loosening during self-diffusion is always higher than during impurity diffusion. The author bases his study chiefly on the vacancy mechanism of diffusion, and explains that the energy of loosening during impurity diffusion is lower than during self-diffusion because the vacancies are formed mainly at sites adjacent to the dissolved atom. When a vacancy is associated with a dissolved atom to form a diatomic molecule, the author describes the possible motion of this molecule through the lattice without the formation of new vacancies. On the basis of this theory, Johnson writes the formula for the coefficient of impurity diffusion as follows:

$$D_x = A e^{-\frac{w+s}{RT}} = A e^{-\frac{Q_x}{RT}}.$$

The author divides the energy of loosening  $Q_x$  into two parts:  $w$  is the energy required to form a vacancy, and  $s$  is the activation energy required to move an atom of the solvent into an adjacent vacancy.

The theory suggested by Johnson is based on an arbitrary assumption on the vacancy mechanism of migration as the only one possible during impurity diffusion. The decrease in the heat of loosening can also be explained by an intensification of any other type of movement (interchange of positions, and interstitial motion) at the sites of the accumulation of

foreign atoms. In addition, sometimes the bonds between the atoms of different metals in the lattice may be stronger than those between atoms of the same metal, and thus the fundamental condition adopted by Johnson is not applicable.

The problem of the mechanism of migration of atoms in the lattice could not be solved by a statistical approach only to the process of diffusion.

To solve this problem, it is apparently necessary to use other methods also. It would be useful to relate this problem to the deformation phenomena taking place in the lattice during self-diffusion, and particularly during impurity diffusion. In such a case it is not possible to consider a single type of migration as the only possible. It can be assumed that all the above types of migration of atoms in the lattice take place to a certain extent.\* It is probable that in each specific case there is a dominating type of motion.

Today, we still do not have sufficient experimental data on self-diffusion and impurity diffusion of metals to solve the problem on the mechanism of the motion of atoms in crystal lattices. We have no data on self-diffusion in crystal lattices containing foreign atoms, the influence of the type of the solid solution formed on the rate of diffusion, the rate of self-diffusion and impurity diffusion at low temperatures, etc. We hope that an experimental study of diffusion will lead to new possibilities for the development of a theory of this phenomenon.

Without any detailed study on the mechanism of motion of atoms in the crystal lattice, it is possible to derive a formula for the temperature dependence of the diffusion coefficient based on the activation energy:

$$D = A e^{-Q/RT}.$$

When solving this problem it is not important which mechanism of motion of atoms is taken as the basis, since this does not influence the temperature dependence of diffusion.

The Frenkel-Braunne formula:

$$D = A - Q/RT$$

can be obtained from the same general theories, irrespective of the nature of the process of the jump of the atom from one equilibrium position to another.

Frenkel /11/ showed that the fundamental factors are the determination of the mean duration  $\tau$  of oscillation of an atom about a single equilibrium position, and the mean distance  $\delta$  between two neighboring equilibrium positions.

For the time  $\tau$  Frenkel derived the following formula:

$$\tau = \tau_0 e^{Q/RT},$$

where  $\tau_0$  is the period of natural oscillation of the atom (value inversely proportional to  $\nu$ , the frequency of oscillation) and  $Q$  is the activation energy of the transition from one equilibrium position to another. The

\* This is confirmed by the existence of interstitial and substitutional solid solutions.

mean distance  $\delta$  can be assumed to be equal to the distance between neighboring atoms.

If we assume that the mean rate of transport of atoms  $v$  is equal to  $\frac{\delta}{\tau}$  and the coefficient of diffusion  $D = \frac{1}{6} v \delta$  (in analogy to the Brownian movement) we obtain:

$$D = \frac{\delta^2}{6\tau} e^{-Q/RT}.$$

Braunne obtained this formula in the same way. It should be pointed out that this formula was derived by Frenkel for diffusion in both solids and liquids.

Polanyi and Wigner /12/ suggested a somewhat different formula for the temperature dependence of the diffusion coefficient in crystalline solids. They regarded the migration of atoms from one equilibrium position to another from the point of view of the interference of the natural oscillations of atoms in the crystal lattice (such processes include uni-molecular reactions, dissociation, evaporation, and diffusion). They found that the formula

$$\tau = \tau_0 e^{\epsilon/kT} = \frac{1}{v} e^{\epsilon/kT}$$

is not very accurate, since it assumes that the amplitudes of oscillation of atoms are statistically independent of one another.

Polanyi and Wigner found that in the case of a one-dimensional transformation (linear lattice), the rate constant of the chemical reaction (or of a similar process, for example diffusion) can be written as follows:

$$K = v e^{-\epsilon/kT}, \quad (*)$$

where  $v$  is the maximum frequency of oscillation;  $\epsilon$  is the energy required to detach an atom; and  $T$  is the absolute temperature. For transformations during the migration of atoms in all three directions (three-dimensional transformation) Polanyi and Wigner wrote formula (\*) as follows:

$$K = \frac{2v}{K'} e^{\epsilon/kT}.$$

Since the value of  $K$  (equal to  $\frac{1}{6\tau}$ ) indicates the number of atoms which interchange position with neighboring atoms per unit time (or statistical probability of such interchange) it can be assumed that in the case of diffusion:

$$D = K \delta^2,$$

where  $\delta$  is the distance between neighboring atoms. Hence, Polanyi and Wigner derived the formula:

$$D = 2 \frac{vQ}{kT} \delta^2 e^{-Q/kT} \quad (**)$$

(i. e.  $A = \frac{2vQ}{kT} \delta^2$ ).

This formula differs from that of Frenkel and Braunne:

$$A = \frac{b^2}{6\tau_0} = \frac{\delta^2 v}{6}.$$

The characteristic feature of this formula is that the coefficient  $A$  depends on temperature (or more accurately on  $Q/T$ ), which cannot, however, greatly influence the diffusion coefficient. \* At low temperatures it can be assumed that  $v = \frac{kT}{h}$ , and then formula (\*\*) can be written as follows:

$$D = \frac{2Q}{Nh} \delta^2 e^{-Q/kT}, \quad (**)^\star$$

where  $N$  is the Avogadro number, and  $h$  is Planck's constant.

Formula (\*\*) is almost identical with the formula of Dushman and Langmuir /13/:

$$D = \frac{Q}{Nh} \delta^2 e^{-Q/RT},$$

which is also derived analogously to the rate of unimolecular reactions.

\* Since in practice  $D$  is measured over a narrow range of temperatures.



## Chapter II

### ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COEFFICIENTS OF SELF-DIFFUSION AND IMPURITY DIFFUSION

#### § 1. Self-diffusion of metals

In Chapter I, § 2, we gave data on the self-diffusion of lead, gold, and copper, which indicate that in all three metals the temperature dependence of the coefficient of self-diffusion is governed by an exponential law:

$$D = Ae^{-Q/RT}.$$

The values of the parameters  $A$  and  $Q$  for these metals are given in Table 1.

TABLE 1.

Metal	$A$ cm <sup>2</sup> /sec	$Q$ cal/mole	Reference
Lead . . . . .	6.7	28,000	3
Gold . . . . .	0.15	53,000	4
		51,000	5
Copper . . . . .	10	57,200	7

We shall compare these data with the formulas derived by different authors for the temperature dependence of diffusion. The chief formulas are as follows:

$$D = Ae^{-Q/RT} = \frac{\delta^2}{6\tau} e^{-Q/RT} \quad (\text{Frenkel}), \quad (1)$$

$$D = Ae^{-Q/RT} = \frac{2\delta^2 v}{RT} Q e^{-Q/RT} \quad (\text{Polanyi and Wigner}) \quad (2)$$

$$D = Ae^{-Q/RT} = \frac{\delta^2}{Nh} Q e^{-Q/RT} \quad (\text{Langmuir and Dushman}) \quad (3)$$

These formulas differ in the value of the coefficient  $A$ . In formulas (1'), (2') and (3')  $A$  is given according to (1), (2), and (3), respectively:

$$A = \frac{\delta^2}{6\tau} = \frac{\delta^2 v}{6}, \quad (1')$$

$$A = \frac{2\delta^2 v}{RT} Q, \quad (2')$$

$$A = \frac{\delta^2}{Nh} Q^* \quad (3')$$

To assess formulas (1'), (2') and (3'), from experimental data, the values of  $A$  were calculated for the self-diffusion of lead, gold and copper. The values of  $\delta$  and  $\nu$  were taken directly from tables, and the heat of loosening  $Q$  was found experimentally (Table 1). For gold  $Q$  is equal to 53,000 cal/mole.

To calculate by means of the Polanyi — Wigner formula,  $A$  was found for two temperatures:  $T = T_s$ , where  $T_s$  is the melting point, and  $T = \frac{1}{2}T_s$ . Table 2 shows how each of the above formulas (1'), (2'), and (3'), satisfies the experimental data. It must be remembered that even in the most favorable case we can expect agreement between the orders of magnitude only, since these formulas do not take into account a number of factors on the structure of real metals.

TABLE 2.  $A, \text{cm}^2/\text{sec}$

Metal	$A = \frac{\delta^2 \nu}{6}$ (Frenkel)	$A = \frac{2\delta^2 \nu}{RT} Q$ (Polanyi and Wigner)	$A = \frac{\delta^2 Q}{Nh}$ (Dushman and Langmuir)	$A_{\text{exp}}$
Lead . . . . .	$3.7 \cdot 10^{-4}$	0.30 — 0.15	0.34	6.7
Gold . . . . .	$5.5 \cdot 10^{-4}$	0.58 — 0.27	0.47	0.15
Copper . . . . .	$7.3 \cdot 10^{-3}$	0.6 — 0.3	0.40	10

Table 2 shows that formulas (2') and (3') give results closest to the experimental, at least as regards the order of magnitude. However, the values of  $A$  calculated from formula (1) are on an average  $10^{-3}$  times the experimental.

Formula (2) of Polanyi and Wigner describes the experimental results fairly well and can be used to find the diffusion coefficient at any temperature from the diffusion coefficient found at some other temperature, that is, to determine the temperature dependence of the diffusion coefficient.

By writing formula (2) in the form:

$$z = q - \ln q, \quad (2'')$$

where

$$q = Q/RT \quad \text{and} \quad z = \ln \frac{\delta^2 \nu}{D},$$

\* To determine the temperature dependence of the diffusion coefficient, Gertsyken and Dekhtyar /14/ suggested that the Dushman-Langmuir formula should not be used (since  $d$  can be about one order of magnitude smaller or larger than the shortest distance between the atoms in the lattice) but rather the Eyring-Wynne-Jones formula /15/:

$$D = e^{\frac{\Delta S}{R}} \cdot \frac{Ed^2}{Nh} \cdot \frac{1}{2.72} e^{-E/RT}$$

or

$$D_0 = e^{\frac{\Delta S}{R}} \cdot \frac{Ed^2}{Nh} \cdot \frac{1}{2.72},$$

where  $e^{\frac{\Delta S}{R}}$  is the entropy of activation.

If this formula is used to determine the diffusion coefficient,  $d$  retains its meaning.

it is possible from the known value of  $D$  at temperature  $T$  to graphically determine the value of  $q$ , and therefore the heat of loosening  $Q$ .

A  $z = q - \ln q$  curve (Figure 1) must be plotted. The point of intersection of this curve with the straight line  $z = \ln \frac{D_0}{D}$  gives the value of  $q$  needed for determining the heat of loosening. This method for finding the heat of loosening during the self-diffusion of various metals from a single value of  $D$  is apparently the simplest.

An analysis of the experimental data showed that an approximate value of  $Q$  can be found even more easily.

The temperature dependence of the coefficient of self-diffusion  $D_s$  of lead, gold, and copper shows that at the melting points these coefficients are so close to one another that they can be considered approximately equal. After we have extrapolated the coefficients of self-diffusion  $D_s$  using the data given in Table 1 we obtain the following values:

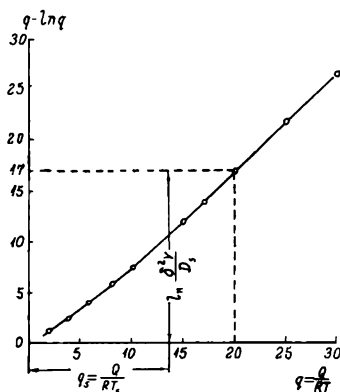


FIGURE 1. Graphical determination of the heat of loosening for self-diffusion.

	$D_s, \text{cm}^2/\text{sec}$
Gold .....	$5 \cdot 10^{-10}$
Lead .....	$5.1 \cdot 10^{-10}$
Copper .....	$10 \cdot 10^{-10}$

The values of  $D_s$  for gold and lead are especially close, despite the great difference between the melting points of these metals.

The equality of the coefficients of self-diffusion at the melting point can be demonstrated well by plotting the following reduced curves of the temperature dependence:

$$D = D_s e^{-\frac{Q}{R} \left( \frac{1}{T} - \frac{1}{T_s} \right)}$$

(i. e.,  $\ln D$  and  $\frac{1}{T} - \frac{1}{T_s}$  coordinates).

These curves are obtained by extrapolating from the data on lead, gold, and copper. They intersect at a single point at  $\frac{1}{T} - \frac{1}{T_s} = 0$ , i. e.,  $\frac{1}{T} = \frac{1}{T_s}$  (Figure 2).

By assuming that the coefficients of self-diffusion at the melting point  $D_s = \text{constant}$ , it is possible to obtain a simple formula for the heat of loosening  $Q$ .

Any of the three known formulas on the coefficient of self-diffusion can be used. We shall, however, apply the formula of Polanyi and Wigner, since it describes the experimental data best, and has been sufficiently well proved. We shall write this formula in the form:

$$\frac{Q}{RT_s} - \ln \frac{Q}{RT_s} = \ln \frac{D_0}{D_s}, \quad (*)$$

where  $T_s$  is the melting point, and  $D_s$  is the coefficient of self-diffusion at this temperature.

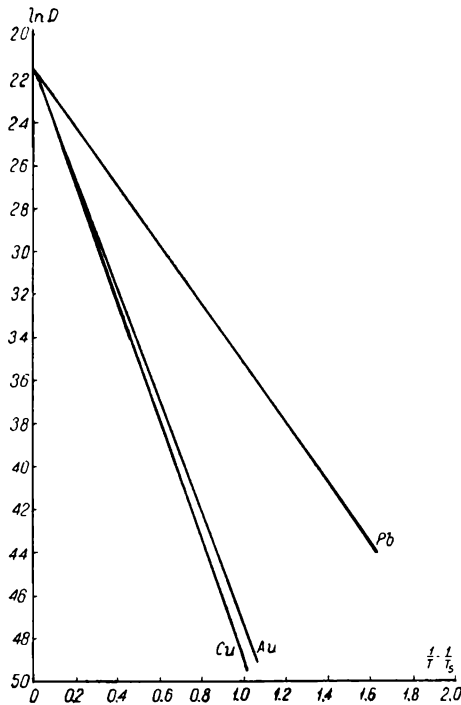


FIGURE 2. Temperature dependence of the coefficients of self-diffusion of Pb, Au, and Cu, calculated from the

reduced formula:  $D = D_s e^{\frac{-Q}{R} \left( \frac{1}{T} - \frac{1}{T_s} \right)}$ .

The values  $\delta^2_v$  are very close for most metals, especially for metals with a face-centered cubic lattice. It can therefore be assumed that  $\delta^2_v = \text{constant}$ , and therefore  $\ln \delta^2_v = \text{constant}$ .

If we also assume that  $D_s = \text{const}$ , from (\*) we obtain:

$$\frac{Q}{RT_s} - \ln \frac{Q}{RT_s} = \text{const}$$

and therefore,

$$\frac{Q}{RT_s} = \text{const},$$

i. e., the heat of loosening is proportional to the temperature of the melting point.

The proportionality factors can be determined from the experimental data. If we assume  $\delta^2_v \cong 3.8 \cdot 10^{-3} \text{ cm}^2/\text{sec}$  and  $D_s \cong 5 \cdot 10^{-10} \text{ cm}^2/\text{sec}$ , we obtain:

$$\ln \frac{\delta^2_v}{D_s} = 17 \quad \text{or} \quad \frac{Q}{RT_s} - \ln \frac{Q}{RT_s} = 17.$$

By solving these equations graphically, and using Figure 1, we obtain:

$$\frac{Q}{RT_s} \cong 20 \quad \text{or} \quad Q \cong 20 RT_s. \quad (**)$$

The formula obtained could be directly checked for lead, gold, and copper, only, as their coefficients of self-diffusion had already been studied.

A comparison between the experimental values of  $Q$  and those calculated from the melting point is shown in Table 3.\*

TABLE 3.

Metal	$Q_{\text{exp}}$	$Q_{\text{calc}} = RT_s$
Lead .....	23,000	24,000
Gold .....	53,000	53,400
Copper .....	57,200	54,240

**General remarks.** An attempt to relate the heat of loosening to the melting point of metals had previously been made by Braunne /8/.

As we have already mentioned, formula (\*\*) could be directly checked from experimental data for three metals only.

However, as we shall see later, this formula could be verified indirectly by using data on the diffusion of atoms of one metal in the lattice of another.

We assumed that  $Q \cong 20 RT_s \cong 40 T_s$ , and obtained values for the heat of loosening of several metals (Table 4).\*\*

The simple relationship between the heat of loosening during the self-diffusion of metals and the melting point agrees with the Braunne theory, which states that the heat of loosening during diffusion is:

$$Q = 3b^2 T_s R,$$

where  $b$  is a certain coefficient, which according to Braunne is close to unity.

From the data we obtained ( $Q = 20 RT_s$ ), the value of  $b$  is about 2.5.

According to Braunne,  $b = \frac{r_0}{r_s}$ , where  $r_0$  is the oscillation amplitude of an atom when it can become detached from its equilibrium position, and  $r_s$  is the mean amplitude of oscillation of atoms at their melting point. Hence, we can assume that the amplitude necessary for interchange of positions should be 2.5 times the mean amplitude of atoms at the melting point. Like the Braunne theory, this conclusion is very approximate.

TABLE 4.

Metal	$T_s$	$Q = 40 T_s$
Nickel .....	1724	68,960
Silver .....	1233	49,320
Platinum .....	2027	81,080
Palladium .....	1826	73,000
Aluminum .....	922	36,880

\* This comparison reaffirms the truth of the assumption that  $D_s = \text{constant}$ .

\*\* In this paper we consider metals with a face-centered lattice only for which formula (\*\*) is apparently the most suitable.

The correctness of our formula  $\frac{Q}{RT_s} = \text{const} \cong 20$  is affirmed also by the great influence of anharmonic oscillations at elevated temperatures. This is because Hooke's law cannot be applied for large oscillation amplitudes. As a result, an increase in the amplitude leads to a shift in the equilibrium position. This has been confirmed by calculation.

In 1913 Debye showed that the thermal expansion of substances is directly related to the anharmonic oscillations. Consequently, the coefficient of linear expansion is a measure of anharmonicity.

The detachment of atoms from their equilibrium positions is also due to the asymmetry of oscillations. This was assumed by Hevesy in 1922 /16/. It can be assumed that the energy  $Q$  necessary to detach an atom is related to the coefficient of expansion.

But the experimental data do not confirm Hevesy's hypothesis /16/. This is because Hevesy did not base his conclusions on the data of self-diffusion, as at that time there were no data except for his own on lead, but on the data of impurity diffusion. This, naturally, could not lead to a simple dependence on the coefficient of expansion. But on the basis of self-diffusion such a relationship can be obtained because of the following considerations: the energy necessary for detaching atoms clearly decreases as the degree of asymmetry of the oscillations increases.

Grüneisen /18/ showed that the heat of loosening  $Q$  is inversely proportional to  $\alpha$ .

At a given temperature  $T$ , this relationship can be written:

$$\frac{Q}{RT} = \frac{A}{\alpha T},$$

where  $A$  is a certain coefficient, or

$$Q = \frac{AR}{\alpha}.$$

The value of the coefficient  $A$  can be found from the data on lead, gold, and copper (Table 5).

TABLE 5. Relationship between the heat of loosening and the coefficient of cubic expansion

Metal	$Q$ cal/mole	$\alpha \cdot 10^4$	$A$
Lead .....	28,000	0.86	1.2
Gold .....	53,000	0.43	1.15
Copper .....	57,200	0.49	1.4

According to Table 5,  $A$  is  $\approx 1.2$  (the fact that the value of  $A$  is close to unity is rather characteristic). Thus, we obtain:

$$Q = \frac{1.2R}{\alpha}.$$

If we know the dependence of  $Q$  on  $T$ , it is easy to find the dependence of  $Q$  on  $T_s$ . It is sufficient to use the theory of Grüneisen, which states that for

most metals

$$\alpha T_s = 0.06 \quad \text{or} \quad \alpha = \frac{0.06}{T_s}.$$

By substituting this value into the formula for  $Q$ , we obtain:

$$Q = \frac{12R}{0.06} T_s = 20 RT_s,$$

which is the same as the formula obtained before from other assumptions.

We should mention the paper of Cichocki in our discussion on the value of  $Q$ . Cichocki suggested a new theory on the self-diffusion of metals /17/.

In this theory it is assumed that the atoms interchanging positions remain for a short time in the same volume that was earlier occupied by a single atom. Hence, it was concluded that the atoms which interchange positions undergo a volume deformation of 50%. From these assumptions, and from his earlier formula, Cichocki gives the following formula for the heat of loosening during self-diffusion:

$$Q = \frac{V_0}{8\chi},$$

where  $V_0$  is the volume of 1 g-atom; and  $\chi$  is the coefficient of hydrostatic stress.

The deformation which atoms undergo during the interchange of positions is a very important factor, and therefore the method chosen by Cichocki for determining the value of  $Q$  deserves serious consideration. However, the value 50% for deformation is quite arbitrary, like the assumption on the existence of 2 atoms in a single site of the lattice. It may preferably be assumed that the atom detached from its equilibrium position will attain a new (temporary) equilibrium position in an interstice close to the regular equilibrium position of another atom, which partially penetrates into its place. This would also lead to local deformation of the lattice. However, this deformation would not be 50% and the calculation is not as simple as Cichocki's.

Cichocki's formula gives values of  $Q$  which satisfactorily agree with the experimental data on the self-diffusion of gold and lead, but the values for copper are much too low (30,900 cal instead of 57,200).

Therefore, it would be interesting to find the relationship between Cichocki's formula  $Q = \frac{V_0}{8\chi}$  and our formula ( $Q = 20 RT_s$ ). The theory of solids /11/ indicates that the value of  $\frac{V_0}{\chi}$  is apparently proportional to the melting point. The relationship between these two values can be determined from the Grüneisen constant /18/  $\gamma = \frac{V\alpha}{c_V\chi}$  (for gold and lead  $\gamma = 3$ ; for copper  $\gamma = 1.96$ ). By adopting this formula and substituting the corresponding values for  $\gamma$ , we obtain

$$\gamma = \frac{V \cdot 0.06}{3R\chi T_s} \quad \text{and} \quad \frac{V}{\chi} = \frac{\gamma 3RT_s}{0.06}.$$

If we assume that for gold and lead  $\gamma=3$ , we obtain

$$\frac{V}{\chi} = 150RT_s^* \quad \text{and} \quad \frac{V}{8\chi} \cong 19RT_s \cong Q,$$

which means that for gold and lead Cichocki's values for  $Q$  are very close to our values ( $Q=20RT_s$ ), and agree well with the experimental data.

If for copper  $\gamma=1.96$ ,  $\frac{V}{\chi} = 98RT_s$ ,

$$\frac{V}{8\chi} \cong 12RT_s \ll Q,$$

i. e., the value of  $Q$  is much smaller than its real value.

## § 2. Diffusion of impurity atoms in crystal lattices

The problems of impurity diffusion are more complex than those of self-diffusion, since the atoms of both solvent and solute migrate simultaneously. The migration of solute atoms is influenced by that of solvent atoms, and the presence of impurity atoms in the lattice changes the energy conditions (degree of loosening), and thus influences the rate of self-diffusion. Although the diffusion of metals has recently been widely studied, the results have not yet been properly processed, and therefore no definite conclusion has been reached. Only Seith and co-workers have qualitatively systematized the experimental results, and we shall discuss them later.

In this section we shall again attempt to systematize the available data on the diffusion of metals to clarify as far as possible: 1) the main factors determining the diffusion coefficient and its temperature dependence; 2) whether it is possible to make an approximate theoretical calculation of the diffusion coefficient; and 3) whether there is a correlation between the heat of loosening during the diffusion of impurity metals and the heat of loosening of the solvent.

Our study will be based chiefly on the paper of Seith and co-workers /19/ on the diffusion of different metals in lead and silver and the papers of Jost /20/ on diffusion in gold. These data were obtained by using very pure metals, and very accurate methods, and are most reliable. The authors (particularly Seith) studied diffusion at low concentrations of impurities, so that the results are especially reliable.

**a) Temperature dependence of impurity diffusion.** We shall consider the published data on the diffusion of metals according to the applicability of the formulas derived by different authors for quantitatively calculating the chief parameters  $A$  and  $Q$ , which determine the temperature dependence of the diffusion coefficient. An experimental determination of the diffusion coefficient  $D$  is considered satisfactory if the error does not exceed 50%. For the theoretically calculated coefficients an even greater error is

\* The expression  $\frac{V}{\chi} = \text{const} \cdot T_s$  can also be obtained from the Frenkel theory of viscosity by comparing his two formulas for the viscosity coefficients.



permissible, and if a calculated diffusion coefficient agrees with an experimental value within one order of magnitude, this is considered satisfactory. The accuracy of the determination of the heat of loosening  $Q$  depends on its absolute value, and in accordance with the high error permissible in the calculation of  $D$ , if the discrepancies do not exceed  $\pm 10-15\%$ , this can be considered satisfactory.

Let us consider which of the formulas on self-diffusion that we have already analyzed can be applied to impurity diffusion:

$$D = \frac{\delta^2 \nu}{6} e^{-Q/RT} \quad (\text{Frenkel, Braunne}),$$

$$D = \frac{2\delta^2 \nu}{RT} Q \cdot e^{-Q/RT} \quad (\text{Polanyi and Wigner}). *$$

According to the Frenkel formula,  $A = \frac{\delta^2 \nu}{6}$ , where  $\delta$  is the distance between atoms in the lattice of the solvent, and  $\nu$  is the maximum vibrational frequency of the atoms of the diffusing metal. In some cases the results are close to the experimental, despite the fact that for self-diffusion of metals this formula is not applicable. The agreement with the experimental results is particularly good for the diffusion of platinum, palladium, and copper in gold, but not so good for the diffusion of different metals in silver. The greatest disagreement with the experimental data was found for the diffusion of some metals in lead. In this case the theoretical data calculated from the formula  $A = \frac{\delta^2 \nu}{6}$  are  $10^2-10^4$  times the experimental.

The results are different if we calculate the values of  $A$  from the formula of Polanyi and Wigner. In this case the results differ least from the experimental data for diffusion in lead, and differ most from the experimental data for diffusion in gold.

Thus, the processes that we have discussed (which produced most of the experimental data on the diffusion of metals) can be divided into two groups. The processes of the first group are characterized by low values of the coefficient  $A$ , and the formula  $A = \frac{\delta^2 \nu}{6}$  cannot be applied to them (diffusion in gold, and partially in silver), but the processes of the second group have high values of  $A$ , and the formula of Polanyi and Wigner

$$D = \frac{2\delta^2 \nu}{RT} Q \cdot e^{-Q/RT}$$

can be applied (diffusion in lead).

As we pointed out in 1937 /21/, this led to the idea that each of these formulas is, apparently, a particular case of a more general formula.

In fact, it is not very probable that these formulas will produce satisfactory results for all cases of interdiffusion of two metals, since they were derived on the basis of the mobility of atoms in lattices of a single metal (i. e., for self-diffusion).

Today, we still have no satisfactory quantitative theory on the migration of impurity atoms in the lattices of metals. Therefore, we have no strictly

\* The formula suggested by Langmuir and Dushman gives results close to those obtained from the Polanyi-Wigner formulas, and therefore we shall not discuss them here.

proved theoretical basis for calculating the constants  $A$  and  $Q$ , which determine the temperature dependence of the coefficient of impurity diffusion.

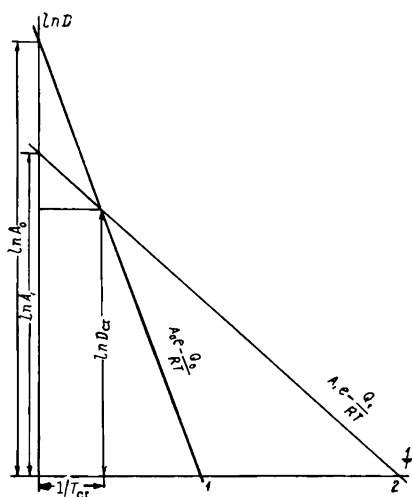


FIGURE 3. Temperature dependence of the coefficients of:

1 — self-diffusion in metals; 2 — impurity diffusion in metals.

However, from certain general ideas it is possible to derive an approximate formula for determining the coefficient  $A$  for the mobility of atoms of one metal in the lattice of another. In such a case we shall assume that the coefficients of self-diffusion, and therefore the constant for self-diffusion, can be satisfactorily determined from the formula of Polanyi and Wigner:

$$D = A_0 e^{-Q_0/RT} = \frac{2\delta^2 v}{RT} Q_0 \cdot e^{-Q_1/RT},$$

i.e.,

$$A_0 = \frac{2\delta^2 v}{RT} \cdot Q_0.$$

As we have already seen, the experimental data confirm these assumptions.

We shall now assume, also on the basis of experimental data, that for the diffusion of atoms of any metal  $B$  (with a maximum vibrational frequency  $v$ ) in the basis metal:

$$Q_0 > Q_1 \quad \text{and} \quad A_0 > A_1,$$

where  $Q_0$  and  $A_0$  are constants of self-diffusion of the basis metal, and  $Q_1$  and  $A_1$  are the corresponding constants for impurity diffusion of metal  $B$  in the basis metal.

If we plot curves of the temperature dependence of the coefficient of self-diffusion  $D_0$  of the basis metal and of the temperature dependence of the coefficient of diffusion  $D_1$  of the metal  $B$  in the basis metal in  $\ln D$  and  $1/T$  coordinates, the curves will intersect at some point at a positive value of  $1/T$  (Figure 3). Let us designate the abscissa of this point as  $1/T_{cr}$ , assuming that  $D_0 = D_1 = D_{cr}$  at a temperature  $T = T_{cr}$ . In such a case, as shown in Figure 3, we can write

$$D_{cr} = A_0 e^{-Q_0/RT} = A_1 e^{-Q_1/RT_{cr}},$$

and hence:

$$A_1 = A_0 e^{\frac{Q_1 - Q_0}{RT_{cr}}}.$$

If we assume that the Polanyi-Wigner formula is correct for self-diffusion, that is:

$$A_0 = \frac{2\delta_y}{RT_{cr}} Q_0,$$

then:

$$A_1 = \frac{2\delta_y}{RT_{cr}} \cdot Q_0 e^{\frac{Q_1 - Q_0}{RT_{cr}}} \quad (1)$$

and

$$D_1 = \frac{2\delta_y}{RT_{cr}} Q_0 e^{\frac{Q_1 - Q_0}{RT_{cr}}} \cdot e^{-\frac{Q_1}{RT}}. \quad (2)$$

These formulas indicate that if the Polanyi-Wigner theory is used for impurity diffusion, in the formula for  $A$ ,  $Q$  (the heat of loosening during impurity diffusion) must be substituted by  $Q_0 e^{\frac{Q_1 - Q_0}{RT_{cr}}}$ .

Formulas (1) and (2) also indicate that during the calculation of the coefficient of diffusion of one metal in another it is necessary to take into account the heat of loosening  $Q_0$  of the solvent metal. In this way, we correlate the process of impurity diffusion with that of self-diffusion.

To use formulas (1) and (2) to calculate  $D$ ,  $A$ , and  $Q$  it was necessary to determine whether it is possible to find a temperature  $T_{cr}$  at which the diffusion coefficients of different metals in the same solvent metal are equal to one another and to the coefficient of self-diffusion of the basis metal.

In analogy with self-diffusion, we could a priori assume that at a sufficiently low concentration of the diffusing metal the temperatures  $T_{cr}$  for different metals in the same solvent metal will not greatly differ, and that this temperature will be close to the melting point of the basis metal. To determine whether this assumption is confirmed by experimental data, we determined the coefficients of diffusion of (different) metals in lead, gold, and silver at their melting points by extrapolating the experimental temperature curves. The results are given in Tables 6, 7 and 8.\*

\* The values of  $D$ , given in these tables were calculated from the formula:  $\ln D = \ln A - \frac{Q}{RT}$ .

Tables 6, 7 and 8 and Figure 4 show that the diffusion coefficients of different metals in the same solvent at its melting point are usually quite close to one another. For diffusion in silver (Table 6), the differences between the diffusion coefficients are very small, and do not exceed the experimental error, even for very accurate measurements. There is also good agreement between the  $D_i$  values for diffusion in gold (except for the diffusion of copper in gold). The results for the diffusion of a number of metals in lead agree less, and the divergencies between individual values of  $D_i$  are greater. However, here also the deviations from the mean value of  $D_i$  do not exceed the order of magnitude of  $D_i$  itself (except for the diffusion of gold and silver in lead). Thus, if we consider the possible variations in  $D_i$  as a result of the influence of different structural factors of the crystal lattice, we can assume that  $T_{cr} = T_i$  when calculating the diffusion coefficients from formula (1).

TABLE 6. Diffusion coefficients of different metals in silver at  $T = T_s$  (1233°C)

Diffusing metal	$Q$ cal	$Q/RT_s$	$A$ cm <sup>2</sup> /sec	$\ln A$	$\ln D_s$	$D_s$ cm <sup>2</sup> /sec
Cadmium . . . .	22,350	8.6	$4.9 \cdot 10^{-5}$	-10.8	-19.4	$4 \cdot 10^{-9}$
Indium . . . . .	21,400	9.4	$7.3 \cdot 10^{-5}$	-11.2	-20.6	$2 \cdot 10^{-9}$
Tin . . . . .	21,400	8.2	$7.9 \cdot 10^{-5}$	-11.3	-19.5	$3.2 \cdot 10^{-9}$
Antimony . . . .	21,700	8.3	$5.3 \cdot 10^{-5}$	-10.9	-19.2	$5 \cdot 10^{-9}$
Copper . . . . .	24,300	9.5	$5.9 \cdot 10^{-5}$	-11.0	-20.5	$1 \cdot 10^{-9}$
Gold . . . . .	29,800	11.4	$5.3 \cdot 10^{-4}$	-8.5	-19.9	$2.5 \cdot 10^{-9}$
Palladium . . . .	20,200	7.7	$6.4 \cdot 10^{-6}$	-13.3	-21.0	$0.8 \cdot 10^{-9}$

TABLE 7. Diffusion of different metals in lead at  $T = T_s$  (600°C)

Diffusing metal	$Q$ cal	$Q/RT_s$	$A$ cm <sup>2</sup> /sec	$\ln A$	$\ln D_s$	$D_s$ cm <sup>2</sup> /sec
Gold . . . . .	14,000	11.7	$3.5 \cdot 10^{-1}$	-1.24	-12.94	$3.2 \cdot 10^{-6}$
Silver . . . . .	15,200	12.7	$7.5 \cdot 10^{-2}$	-3.30	-16	$1 \cdot 10^{-7}$
Cadmium . . . .	15,400	12.9	$1.9 \cdot 10^{-3}$	-6.21	-19.1	$6.3 \cdot 10^{-9}$
Mercury . . . . .	19,000	17.7	$3.6 \cdot 10^{-1}$	-1.29	-19.0	$6.3 \cdot 10^{-9}$
Tin . . . . .	26,200	21.8	4.1	-1.40	-20.4	$1.3 \cdot 10^{-9}$
Thallium . . . .	19,400	16.1	$2.6 \cdot 10^{-2}$	-3.24	-19.3	$6.3 \cdot 10^{-9}$
Bismuth . . . . .	18,400	15.3	$1.9 \cdot 10^{-2}$	-2.94	-18.2	$10 \cdot 10^{-9}$
Lead (self-diffusion . . . .	28,000	23.3	6.7	-1.9	-21.4	$0.5 \cdot 10^{-9}$

TABLE 8. Diffusion of different metals in gold at  $T = T_s$  (1336°C)

Diffusing metal	$Q$ cal	$Q/RT_s$	$A$ cm <sup>2</sup> /sec	$\ln A$	$\ln D_s$	$D_s$ cm <sup>2</sup> /sec
Platinum . . . .	39,000	14.6	$12.4 \cdot 10^{-4}$	-6.7	-21.3	$5.8 \cdot 10^{-10}$
Palladium . . .	37,400	14	$11.1 \cdot 10^{-4}$	-6.8	-20.8	$9.2 \cdot 10^{-10}$
Copper . . . . .	27,400	10.2	$5.8 \cdot 10^{-4}$	-7.4	-19.6	$18 \cdot 10^{-9}$
Gold (self-diffusion . . . .	53,000	19.8	$1.5 \cdot 10^{-1}$	-1.8	-21.6	$5.1 \cdot 10^{-10}$

For comparison, Tables 9—11 give the values of  $A$  obtained experimentally and by calculation from the formulas of Frenkel, Polanyi and Wigner and from our formula (1).

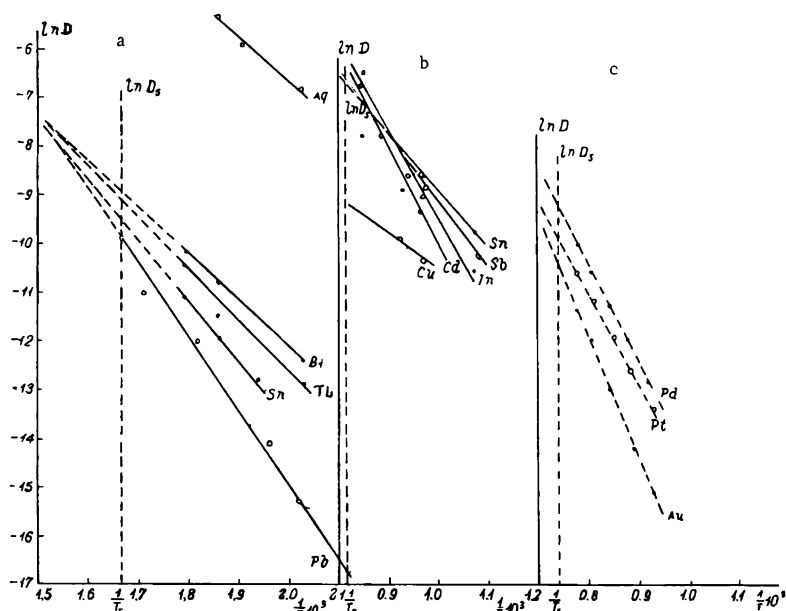


FIGURE 4. Temperature dependence of the diffusion coefficients of different metals:

a—in lead (according to Seith); b—in silver (according to Seith); c—in gold (according to Jost).

To determine  $A$  from (1), we used experimental data on the heat of loosening  $Q_0$  during self-diffusion, and the heat of loosening  $Q_1$  during the diffusion of different foreign metals.

TABLE 9. Values of  $A$  for diffusion in gold

Diffusing metal	$A_{\text{exp}}$	$A_{\text{calc}}$		
		formula of Frenkel ( $A = \frac{2k^2v}{6}$ )	formula of Polanyi and Wigner ( $A = \frac{2k^2v}{RT} \cdot Q$ )	calc. from formula (1) ( $A = \frac{2k^2v}{RT_s} \cdot Q_0 e^{(Q_1 - Q_0)/RT_s}$ )
Platinum . . . .	$5.0 \cdot 10^{-4}$	$11.7 \cdot 10^{-4}$	$1.02 \cdot 10^{-1} - 2.04 \cdot 10^{-1}$	$8.7 \cdot 10^{-4}$
Palladium . . . .	$11.1 \cdot 10^{-4}$	$15.6 \cdot 10^{-4}$	$1.31 \cdot 10^{-1} - 2.62 \cdot 10^{-1}$	$4.7 \cdot 10^{-4}$
Copper . . . . .	$12.4 \cdot 10^{-4}$	$18.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-1} - 2.2 \cdot 10^{-1}$	$1.3 \cdot 10^{-5}$

TABLE 10. Values of  $A$  for diffusion in silver

Diffusing metal	$A_{\text{exp}}$	$A_{\text{calc}}$		
		formula of Frenkel ( $A = \frac{2k^2v}{6}$ )	formula of Polanyi and Wigner ( $A = \frac{2k^2v}{RT} \cdot Q$ )	calc. from formula (1) ( $A = \frac{2k^2v}{RT_s} \cdot Q_0 e^{(Q_1 - Q_0)/RT_s}$ )
Cadmium . . . .	$4.9 \cdot 10^{-5}$	$2.9 \cdot 10^{-4}$	$5.4 \cdot 10^{-2} - 10.8 \cdot 10^{-2}$	$0.6 \cdot 10^{-5}$
Indium . . . . .	$7.3 \cdot 10^{-5}$	$6.2 \cdot 10^{-4}$	$3.6 \cdot 10^{-2} - 7.2 \cdot 10^{-2}$	$1.2 \cdot 10^{-5}$
Tin . . . . .	$7.9 \cdot 10^{-5}$	$10 \cdot 10^{-4}$	$5.2 \cdot 10^{-2} - 10.4 \cdot 10^{-2}$	$0.4 \cdot 10^{-5}$
Antimony . . . .	$5.3 \cdot 10^{-5}$	$8.3 \cdot 10^{-4}$	$4.4 \cdot 10^{-2} - 8.8 \cdot 10^{-2}$	$0.4 \cdot 10^{-5}$
Copper . . . . .	$5.9 \cdot 10^{-5}$	$1.8 \cdot 10^{-3}$	$1.1 \cdot 10^{-1} - 2.2 \cdot 10^{-1}$	$1.2 \cdot 10^{-5}$

Since no experimental data on  $Q_0$  could be found for diffusion in silver, we assumed that  $Q_0 = 20RT_s$ , where  $T_s$  is the melting point of silver.

These tables indicate that for diffusion in gold and silver, results closest to the experimental can be found by calculating  $A$  from formula (1). This formula gives greater disagreement with the experimental data for the impurity diffusion in lead. Good agreement was obtained for the diffusion of tin in lead. For other metals the error was within one order of magnitude. This can be explained by the fact that, as indicated in Table 7 and Figure 4, the diffusion coefficients of different metals in lead at its melting point differ appreciably, and therefore the temperature  $T_{cr}$  at which the temperature curves intersect lies above the melting point. But even in this case formula (1) gives values closer to the experimental than the formula  $A = \frac{\delta^2 v}{6}$ , and on an average the same discrepancies (except for the diffusion of gold and silver in lead) as the Polanyi-Wigner formula. It is characteristic that in this case the experimental data lie between those calculated from formula (2) and from the Polanyi-Wigner formula.

TABLE 11. Values of  $A$  for diffusion in lead

Diffusing metal	$A_{exp}$	$A_{calc}$		
		formula of Frenkel ( $A = \frac{\delta^2 v}{6}$ )	formula of Polanyi and Wigner ( $A = \frac{2\delta^2 v}{RT} \cdot Q$ )	calc. from formula (1) ( $A = \frac{2\delta^2 v}{RT_s} \cdot Q_0 e^{(Q_1 - Q_0)/RT_s}$ )
Gold . . . . .	$3.5 \cdot 10^{-1}$	$16.2 \cdot 10^{-4}$	$2.28 \cdot 10^{-1} - 4.56 \cdot 10^{-1}$	$8 \cdot 10^{-5}$
Silver . . . . .	$7.5 \cdot 10^{-2}$	$20.3 \cdot 10^{-4}$	$3.0 \cdot 10^{-1} - 6.0 \cdot 10^{-1}$	$1.2 \cdot 10^{-4}$
Cadmium . . . .	$1.9 \cdot 10^{-3}$	$14.4 \cdot 10^{-4}$	$2.2 \cdot 10^{-1} - 4.4 \cdot 10^{-1}$	$1.2 \cdot 10^{-4} - 2.2 \cdot 10^{-4}$
Mercury . . . . .	$3.6 \cdot 10^{-1}$	$8.14 \cdot 10^{-4}$	$1.6 \cdot 10^{-1} - 3.2 \cdot 10^{-1}$	$2.6 \cdot 10^{-3} - 4 \cdot 10^{-3}$
Tin . . . . .	4.1	$14.5 \cdot 10^{-4}$	$3.6 \cdot 10^{-1} - 7.2 \cdot 10^{-1}$	4 - 2
Thallium . . . .	$2.6 \cdot 10^{-2}$	$8.5 \cdot 10^{-4}$	$1.6 \cdot 10^{-1} - 3.2 \cdot 10^{-1}$	$4 \cdot 10^{-3}$
Bismuth . . . . .	$1.8 \cdot 10^{-2}$	$6.7 \cdot 10^{-4}$	$1.2 \cdot 10^{-1} - 2.4 \cdot 10^{-1}$	$2.2 \cdot 10^{-3}$

Our analysis of the experimental data explains why a formula that cannot be applied to any of the known three cases of self-diffusion sometimes gives satisfactory results for the diffusion of one metal in another. In fact, this formula can be considered to be a particular case of formula (2), assuming that  $T_{cr} = T_s$ :

$$A = \frac{2\delta^2 v}{RT_s} Q_0 e^{\frac{Q_1 - Q_0}{RT_s}},$$

when the process of diffusion of two metals satisfies the condition:

$$\frac{2\delta^2\nu}{6} = \frac{2\delta^2\nu}{RT_s} Q_0 e^{\frac{Q_1 - Q_0}{RT_s}}$$

or

$$2 \frac{Q_0}{RT_s} e^{\frac{Q_1 - Q_0}{RT_s}} = \frac{1}{6}.$$

If we assume that

$$\frac{Q_0}{RT_s} \cong 20,$$

we obtain

$$e^{\frac{Q_1 - Q_0}{RT_s}} = \frac{1}{240} \text{ and } \frac{Q_0 - Q_1}{RT_s} \cong 6. \quad *$$

This is the necessary condition for the application of the Frenkel formula.

The expression obtained indicates that the Frenkel formula holds better when the term  $RT_s$  is large, i. e., when the melting point of the basis metal is high. For example, the best results are obtained for the diffusion of platinum and palladium in gold, when

$$Q_0 - Q_1 \cong 15,000 \text{ cal/mole} \quad \text{and} \quad RT_s \cong 2700, \quad \text{i. e.,}$$

$$\frac{Q_0 - Q_1}{RT_s} \cong 6.$$

The experimental data we have discussed here could be supplemented by the data of Mehl and Rhines /22/ on the diffusion of different metals in copper. However, due to the lack of tables and of numerical values of  $A$  and  $Q$  this paper is difficult to apply, and the determination of the corresponding values from the numerous curves illustrating the results of this study can lead to considerable errors. Therefore, we can only use the results on the diffusion in copper to see whether (2) can be applied in this case also.

Mehl and Rhines indicate that the Dushman-Langmuir formula cannot be applied to their data and illustrate this by the following example. The diffusion coefficients of certain metals (zinc, aluminum and beryllium) in copper at 800°C is equal to  $D_{800} = 4 \cdot 10^{-10} \text{ cm}^2/\text{sec}$ . The Dushman-Langmuir formula gives the value of  $Q$  as 44,000 cal/mole, and the experimental value of  $Q$  is 39,000 cal/mole. Since the Dushman-Langmuir formula is essentially very similar to the Polanyi-Wigner, we introduced a correction, and used the above data of Mehl and Rhines to determine  $Q$  from formula (2):

$$D = \frac{2\delta^2\nu}{RT_s} \cdot Q_0 e^{\frac{Q_1 - Q_0}{RT_s}} \cdot e^{-\frac{Q_1}{RT_s}},$$

where  $\delta$ ,  $\nu$ , and  $T_s$ , are the lattice parameter, the maximum oscillation frequency, and the melting point of pure copper, respectively;  $Q_0$  is the heat of loosening during the self-diffusion of copper; and  $Q_1$  is the required value of the heat of loosening during the diffusion of zinc and beryllium in copper.

\* As the value of  $Q_0 - Q_1$  is considerably higher than  $RT_s$ .

Since  $A_0 = \frac{28^2 \nu}{RT_s} Q_0 = 10 \text{ cm}^2/\text{sec}$ , \* after substituting  $T_c$  by  $T_s$ , equation (2) can be written:

$$\ln D = \ln A_0 - \frac{Q_0}{RT_s} + \frac{Q_i}{R} \left( \frac{1}{T_s} - \frac{1}{T} \right).$$

As we have already shown  $\frac{Q_0}{RT_s} \cong 20$ . According to Mehl, at  $800^\circ\text{C}$  (or  $T = 1073^\circ$ ),  $D = 4 \cdot 10^{-10} \text{ cm}^2/\text{sec}$ .

The value of  $Q$  can be found by substituting all known values into the above equation. After these calculations it appeared that  $Q = 39,000 \text{ cal/mole}$ , which is exactly the value obtained experimentally by Mehl and Rhines.

We have discussed different formulas for calculating diffusion coefficients, and have chosen the value of the coefficient  $A$  as a criterion for their applicability. Since  $A$  and  $Q$  are correlated, the same conclusions on the agreement between the calculated and the experimental values of  $A$  can be applied to  $Q$ . However, since the heat of loosening  $Q$  is the fundamental and most important characteristic of diffusion, a direct comparison between the calculated and experimental values of  $Q$  is of great interest.

We chose the following method.

Earlier authors took different  $Q_0$  values obtained for self-diffusion of the solvent metal, and from (1) calculated  $A$  for the diffusion of different metals in this solvent. We, however, shall start with the experimental values of  $A$  and  $Q$  for the diffusion of different metals in lead, gold, and silver, and from (1) find the values of  $Q_0$  for the self-diffusion of the solvent metal. Thus, for each solvent metal we shall obtain not only one but a number of values of  $Q_0$  (depending on the data available on the diffusion of different metals in a given solvent). The agreement between the calculated and the experimental values will indicate how correctly (1) correlates the heat of loosening during the diffusion of different metals to the heat of loosening during the self-diffusion of the solvent metal. It should be pointed out that in the case of silver it is impossible to compare the calculated values of  $Q_0$  with experimental, since no such data exist and the data obtained from (1) can only be compared to those calculated from our formula for self-diffusion,  $Q_0 = 20 RT_s$ .

To convert (1) into the most convenient form for this purpose, the following transformation should be carried out:

$$A_i = \frac{28^2 \nu}{RT_s} Q_0 e^{\frac{Q_i - Q_0}{RT_s}},$$

where  $Q_0$  is the heat of loosening during self-diffusion;  $Q_i$  is the heat of loosening during impurity diffusion,  $T_s$  is the melting point of the solvent metal:

$$\begin{aligned} \ln A_i &= \ln (28^2 \nu) + \ln \frac{Q_0}{RT_s} + \frac{Q_i}{RT_s} - \frac{Q_0}{RT_s}; \\ \frac{Q_0}{RT_s} - \ln \frac{Q_0}{RT_s} &= \ln (28^2 \nu) - \ln A_i + \frac{Q_i}{RT_s}. \end{aligned} \quad (3)$$

\* According to the data of Steigman, Shockley, and Nix.



This equation is analogous to that we have already derived for the self-diffusion of metals (see p. 15) where we substituted the value  $D_s$  the coefficient of impurity diffusion at the melting point for  $\ln A_i - \frac{Q_i}{RT_s}$ .

If from experimental data we know the values of the  $A_i$  coefficient and the heat of loosening  $Q_i$ , in each case of diffusion the left-hand side of (3) can be determined graphically from the curve in Figure 1, and thus the value of  $Q_0$ .

Values of  $Q_0$  for the self-diffusion of lead, gold, and silver, calculated in this way are given in Tables 12, 13, and 14, respectively. For comparison, these tables also give the values of  $Q_0$  obtained experimentally and calculated from the formula.

These tables indicate that there is good agreement between the values of  $Q_0$  for the self-diffusion of any metal calculated from the data obtained for the diffusion of a number of other metals in the same solvent metal.

Hence, it can be concluded that (1) and (3) used for the calculations correctly describe the relationships between the rates of diffusion of different metals in a single solvent metal. Therefore, the fundamental assumption on the intersection of the curves representing the temperature dependence of diffusion at a single point is adequately proved.

TABLE 12. Calculated values of  $Q_0$  for lead.  $Q_{0\text{exp}} = 28,000$  cal/mole;  $Q_0 = 20 RT_s = 24,000$  cal/mole

Diffusing metal	$A$ cm <sup>2</sup> /sec	$\ln A$	$Q_1$	$\frac{Q_1}{RT_s}$	$c = \ln 26^2 v_0 - \ln A + Q_1/RT_s$	$\frac{Q_0}{RT_s}$ (from curve)	$Q_0$
Cadmium . . . . .	$1.9 \cdot 10^{-8}$	-6.21	15,400	12.9	13.7	17	20,400
Mercury . . . . .	$3.6 \cdot 10^{-1}$	-1.0	19,000	17.7	13.7	17	20,400
Tin . . . . .	4.1	1.4	26,200	21.8	17.8	21	25,200
Thallium . . . . .	$2.6 \cdot 10^{-2}$	-3.68	19,400	16.1	14.7	18	21,600
Bismuth . . . . .	$1.9 \cdot 10^{-2}$	-3.91	18,400	15.3	13.8	17	20,400
Lead . . . . .	6.7	+1.84	28,000	23.3	20.8	23	20,000
Mean . . . . .	—	—	—	—	—	—	23,000

A comparison between the calculated mean values of  $Q_0$  and the experimental values shows that there are certain differences but these do not exceed 20%. The greatest difference (about 20%) was found for diffusion in lead, and the smallest difference (close to zero) for diffusion in gold. As we have already mentioned, for silver we could only compare the calculated values with other values calculated from the formula  $Q_0 = 20RT_s$ . The mean differences were about 15%. One of the reasons for these differences between the calculated and experimental values is that the point of intersection of the curves does not always coincide with the melting point of the solvent metal, although it lies very close to it.

TABLE 13. Calculated values of  $Q_0$  for gold.  $Q_{0\text{exp}} = 53,000$ ;  $Q_0 = 20 RT_s = 53,000$  cal/mole

Diffusing metal	$A$ cm <sup>2</sup> /sec	$\ln A$	$Q_1$	$\frac{Q_1}{RT_s}$	$c = \ln 28^2 v_0 -$ $-\ln A + \frac{Q_1}{RT_s}$	$\frac{Q_0}{RT_s}$ (from curve)	$Q_0$
Platinum . . . . .	$5.8 \cdot 10^{-4}$	-7.6	39,000	14.6	17.2	19.5	53,440
Palladium . . . . .	$11.1 \cdot 10^{-4}$	-6.8	37,400	14.0	15.8	18	51,000
Gold . . . . .	1.4	-1.9	53,000	0.20	17.8	20	55,000
Copper . . . . .	$12.4 \cdot 10^{-4}$	-6.7	27,400	10.2	—	12	— <sup>*</sup>
Mean . . . . .	—	—	—	—	—	—	53,000

\* The value of  $Q_0$  calculated from the data on the diffusion of Cu in Au is not given, since it is much too low. This is, apparently, because of the inaccurate values of  $Q$  and  $A$  for the diffusion of Cu in Au.

TABLE 14. Calculated values of  $Q_0$  for silver.  $Q_0 = 20 RT_s = 48,000$  cal/mole

Diffusing metal	$A$ cm <sup>2</sup> /sec	$\ln A$	$Q_1$	$\frac{Q_1}{RT_s}$	$c = \ln 28^2 v_0 -$ $-\ln A + \frac{Q_1}{RT_s}$	$\frac{Q_0}{RT_s}$ (from curve)	$Q_0$
Cadmium . . . . .	$4.9 \cdot 10^{-5}$	-9.9	22,350	8.6	13.7	17	42,000
Indium . . . . .	$7.3 \cdot 10^{-5}$	-9.4	24,400	9.4	13.2	17	42,000
Tin . . . . .	$7.9 \cdot 10^{-5}$	-9.4	21,400	8.2	12.7	16	39,500
Antimony . . . . .	$5.3 \cdot 10^{-5}$	-9.8	21,700	8.3	13.7	17	42,000
Copper . . . . .	$5.9 \cdot 10^{-5}$	-9.7	24,800	9.5	14.3	17.6	43,000
Gold . . . . .	$5.3 \cdot 10^{-5}$	-7.5	29,800	11.4	14.3	17.5	23,000
Palladium . . . . .	$6.4 \cdot 10^{-5}$	-12	20,200	7.7	14.8	18	44,000
Mean . . . . .	—	—	—	—	—	—	42,000

b) Dependence of the heat of loosening during impurity diffusion on the atomic properties of the diffusing metal. From the above conclusions on the temperature dependence of the coefficient of impurity diffusion, no quantitative determination of the heat of loosening  $Q$  is possible. This most important characteristic of the process can be determined experimentally only. However, it is possible to determine from experimental data which properties of the impurity metal are the most important and govern the value of  $Q$  and the coefficient of impurity diffusion.

At present, one of the best proved conclusions which can be drawn is that during the diffusion of several impurities in a single solvent metal, the heat of loosening is highest (and therefore the diffusion coefficient at a given temperature is lowest) for the self-diffusion of the solvent metal. This assumption is confirmed by the above tables of the fundamental constants for the diffusion of different metals in lead (according to Seith and co-workers) and in gold (according to Jost), and also by a later work of Mehl on diffusion in copper.

Tables 12 and 13 show that the heat of loosening during self-diffusion of a metal is considerably higher, sometimes by 100%, than the heat of loosening during impurity diffusion in the same metal.

The same tables give the  $Q_1/RT_s$  ratios ( $T_s$  is the melting point of the solvent metal), which like the  $Q_1$  values vary over a wide range. Thus, the conclusion of Braunne that  $Q/RT_s = 3b^2$ , where  $b^2$  is close to unity, is not true for impurity diffusion.\*

For self-diffusion  $Q/RT_s = \text{constant}$ , and therefore the melting point is the chief factor determining the value and the temperature dependence of the coefficient of self-diffusion. But in impurity diffusion the melting point only influences the coefficient of impurity diffusion, and does not determine it.

Seith /19/ processed the data of himself and his co-workers on diffusion in lead and silver, and concluded that at a given temperature the heat of loosening, or the coefficient of impurity diffusion, depends on the chemical affinity of the impurity metal to the solvent metal.

Seith ordered the impurity metals diffusing into the same metal according to their position in the periodic table, and found, that the farther the impurity metal lies from the solvent metal, the greater is its rate of diffusion and the lower its heat of loosening  $Q$ .

Thus, for diffusion in lead, the heat of loosening increases from silver, which is farthest from lead, to tin (fifth period) which is closest to it, and from gold to bismuth (sixth period). Seith explains the minimum heat of loosening for self-diffusion from the same point of view.

Seith therefore emphasizes the great importance in diffusion of the structure of the electron shells of the impurity metals and the number of their valence electrons.

Seith admits that other properties of the atoms, including their dimensions, can also influence impurity diffusion, but he believes these are less important.

Although Seith's theory is well-founded, it is analogous to the Hume-Rothery theory /29/ on the role of the relative valence in the formation of solid solutions, and we have no definite proof that the relative valence is the only or even the dominating factor influencing the rate of impurity diffusion.

The periodicity in the variation in the coefficients of impurity diffusion (or in  $Q$ ) can also be explained by the influence of some properties of the impurity metal which also vary periodically. This explanation is quite justified, since many properties of solid metals, including the atomic radius, vary periodically. Thus, the diffusion of different metals in lead can be explained by the difference between the atomic dimensions of the impurity metals.

\* Braunne assumes that this ratio is also true for self-diffusion.

It seems to be quite natural that the atomic dimensions should considerably influence the rate of impurity diffusion, and consequently the heat of loosening.

The deformation of the lattice caused by the impurity atoms, and consequently the heat of loosening, depend on the atomic dimensions.

We arrived at this conclusion in 1936 /21/ after analyzing the experimental results on metal diffusion. At that time, we expressed the dependence of  $Q$  on the atomic dimensions by the formula

$$Q = ar^2,$$

where  $a$  is a constant and  $r$  is the atomic radius of the impurity metal.\*

The  $Q = ar^2$  formula seems to indicate that  $Q$  will not be highest for self-diffusion if the atomic radius of one of the impurity metals is larger than the radius of the solvent metal. However, the most recent data on the self-diffusion of gold and copper and on the diffusion of other metals in copper indicate that even if the radius of the impurity metal is greater than that of the solvent metal, the heat of loosening is highest for self-diffusion. Consequently, the  $Q = ar^2$  formula has not been confirmed experimentally. In addition, we now believe that our formula should be written

$$Q = f(V_0 - V),$$

where  $V_0$  is the volume of a one gram-atom of the solvent metal; and  $V$  is the volume of one gram-atom of impurity metal (for calculations, the absolute values of  $V_0 - V$  should be taken).

To verify this formula we used existing data on the distribution of different metals in lead, gold, and silver, plotted on curves in  $Q$ ,  $(V_0 - V)$  coordinates. The corresponding data are given in Tables 15, 16, and 17;  $Q = f(V_0 - V)$  curves are shown in Figure 5.

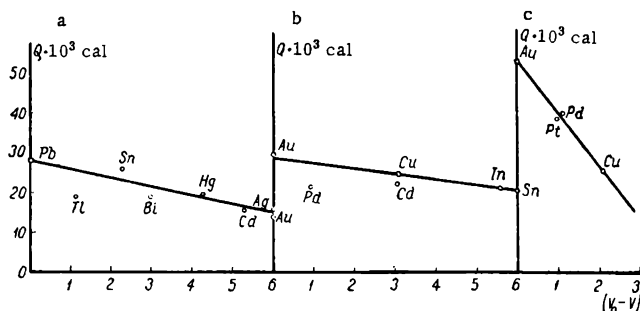


FIGURE 5. Dependence of the heat of loosening  $Q$  on the atomic volumes of impurity metals:

a — diffusion in lead; b — diffusion in silver; c — diffusion in gold.

\* We shall designate by  $r$  the atomic radius according to Goldschmidt, i.e., calculated from the coordination number 12.

These tables (particularly Tables 15 and 16 for diffusion in lead and gold) show that, except for some individual cases, the values of  $Q$  increase with decrease in the difference between the atomic volumes of the impurity and solvent metals ( $V_0 - V$ ), and that  $Q$  is highest at  $V_0 - V = 0$ , that is for self-diffusion of metals.

Figure 5 shows that the points representing different metals diffusing in the same solvent metal lie on a straight line, irrespective of the sign of ( $V_0 - V$ ). It is important that for diffusion in gold and lead the values of  $Q$  corresponding to the self-diffusion of these metals (at  $V_0 - V = 0$ ) lie on the same straight lines. For these two metals we can write our formula:

$$Q_0 = Q + a(V_0 - V)$$

or

$$Q = Q_0 - a(V_0 - V), \quad (a)$$

where  $a$  is a coefficient which depends on the slope of the straight line  $Q = f(V_0 - V)$ .

TABLE 15. Diffusion in lead.  $Q_0 = 28,000$  cal/mole;  $\chi = 23.7 \cdot 10^{-7}$  cm<sup>2</sup>/kg;  $V_0 = 18.3$  cm<sup>3</sup>

Diffusing metal	$V$	$ (V_0 - V) $	$Q$	$Q_0 - Q$	$a = \frac{Q_0 - Q}{ (V_0 - V) }$	$b = \frac{1}{a\chi}$
Gold .....	10.2	6.1	14,000	14,000	$2.3 \cdot 10^3$	4.3
Silver .....	10.2	6.1	15,200	12,800	$2.1 \cdot 10^3$	4.7
Cadmium .....	13	5.3	15,400	12,600	$2.3 \cdot 10^3$	4.3
Mercury .....	14.3	4.3	19,000	11,000	$2.8 \cdot 10^3$	4.5
Tin .....	16.3	2	26,200	1,800	$0.9 \cdot 10^3$	1.1
Thallium .....	17.2	1.1	19,400	8,600	$7.8 \cdot 10^3$	1.3
Bismuth .....	21.3	3.0	18,400	9,600	$3.2 \cdot 10^3$	3.1
Lead .....	18.3	0	28,000	0	—	—

TABLE 16. Diffusion in gold.  $Q_0 = 53,000$ ;  $V_0 = 10.2$  cm<sup>3</sup>;  $\chi = 5.8 \cdot 10^{-7}$  cm<sup>2</sup>/kg

Diffusing metal	$V$	$ (V_0 - V) $	$Q$	$Q_0 - Q$	$a = \frac{Q_0 - Q}{ (V_0 - V) }$	$b = \frac{1}{a\chi}$
Copper .....	7.1	3.1	27,400	25,600	$0.83 \cdot 10^4$	4.8
Palladium .....	9.3	0.9	37,400	15,600	$1.6 \cdot 10^4$	2.5
Platinum .....	9.1	1.1	39,000	14,000	$1.2 \cdot 10^4$	3.3
Gold .....	10.2	0	53,000	0	—	—

TABLE 17. Diffusion in silver.  $Q_0 = 48,000$ ;  $V_0 = 10.2$  cm<sup>3</sup>

Diffusing metal	$V$	$(V_0 - V)$	$Q$	Diffusing metal	$V$	$(V_0 - V)$	$Q$
Cadmium .....	13.0	2.8	22,350	Gold .....	10.2	0	29,800
Indium .....	15.8	5.6	21,400	Palladium .....	9.2	1.0	20,200
Tin .....	16.3	6.1	21,400	Silver .....	10.2	0	
Copper .....	7.1	3.1	24,300				

The coefficients  $a$  are given in Tables 15 and 16. The values of these coefficients for a given solvent metal are almost constant.

The term  $a(V_0 - V)$  in formula (a) represents an additional energy of loosening of the lattice, which is the result of elastic deformation caused by the penetration of an impurity atom. Hence, it can be assumed that the coefficient  $a$  is related to a constant characterizing the elastic properties of the basis metal, for example, to the coefficient of hydrostatic stress,  $\chi$ . This is also confirmed by the fact that the dimensions of the term  $a(V_0 - V)$  should be the same as those of energy, and consequently the dimensions of the coefficient  $a$  should be the same as those of stress.

If we assume:

$$a = \frac{1}{b\chi} \quad \text{and} \quad a(V_0 - V) = \frac{V_0 - V}{b\chi} \cdot 2.4 \cdot 10^{-2},$$

where  $b$  is a certain abstract coefficient, we can write formula (a) as:

$$Q = Q_0 - \frac{(V_0 - V)}{b\chi} \cdot 2.4 \cdot 10^{-2}. \quad (b)$$

(The coefficient  $2.4 \cdot 10^{-2}$  is introduced to express  $(V_0 - V)$  in  $\text{cm}^3$  and  $\chi$  in  $\text{cm}^2/\text{kg}$ ).

Since the values of  $\chi$  are known for all metals, it is possible to determine the coefficient  $b$ , if we take  $\chi$  as the coefficient of hydrostatic stress for the solvent metal.\* The values of the coefficient  $b$  for the diffusion of various metals in lead and gold are given in Tables 15 and 16.

If we disregard the data on the diffusion of tin and thallium in lead, it can be seen that the coefficient  $b$  changes little, and it can be considered constant not only for the same solvent but also for other solvent metals.

We have considered the values of  $\chi$  related to the volume of one gram-atom of metal in the free state. However, during diffusion the atoms of impurity metals become compressed, and their volume decreases. According to Biltz /24/, this decrease in volume is noticeable for alkaline and alkaline-earth metals only, and can be disregarded in our study.

Thus, the heat of loosening during impurity diffusion can be considered to be equal to the heat of loosening  $Q_0$  during self-diffusion minus a value proportional to the difference between the atomic volumes of the diffusing metals.

Thus, the temperature dependence of the coefficient of impurity diffusion can be written:

$$D = Ae^{-Q/RT} = Ae^{-\frac{(Q_0 - Q')}{RT}},$$

where  $Q_0$  is the heat of loosening for self-diffusion, and  $Q' = \frac{V_0 - V}{b\chi} \cdot 2.4 \cdot 10^{-2}$  is the increase in the heat of loosening the lattice as a result of the penetration of impurity atoms. The theories discussed above should be considered as a framework which illustrates the influence of the atomic volume of impurity metals on the rate of impurity diffusion.

\* The values of  $\chi$  were taken from the data of Borelius in the "Encyclopedia of Metal Physics," Vol. I.

### *Chapter III*

#### *DIFFUSION AND STRUCTURE OF METALS*

In the last chapter we discussed diffusion without taking into account the influence of the crystal structure of metals on this process. This did not prevent us from coming to a number of generalized conclusions on the absolute values of the diffusion coefficient  $D$  and on the values of the heat of loosening  $Q$ . As we shall see later, the values of  $Q$  are little influenced, by the crystal structure (for example, by the grain size in polycrystalline aggregates). The absolute values of the diffusion coefficients, and also of the coefficient  $A$  in the formula for the temperature dependence of the diffusion coefficient, are greatly influenced by the structural properties, and therefore these values can be obtained correct to within one order of magnitude only.

By using our own experimental data, in this chapter we shall discuss the influence of some structural factors on the diffusion coefficient and its temperature dependence.

For a more detailed study on this problem, we shall use data on diffusion in metals and the related phenomenon of the electrolytic conductivity of solid salts.

As we have already mentioned, the migration of atoms or ions in a crystal lattice is manifested as diffusion of material or as electrolytic (ionic) conductivity.

These are two different aspects of the same process, and therefore they are closely correlated.

If at a given temperature the current carriers are ions of the same sign, the temperature dependence of the electrolytic conductivity is given by a formula similar to that for diffusion:

$$K = Ae^{-E/RT},$$

where  $K$  is the conductivity;  $E$  is the energy for the detachment of an ion from its equilibrium position in the lattice.  $E$  is of the same order of magnitude as  $Q$  in the diffusion of metals. Also,  $E$  is often influenced by the same factors as  $Q$ . Finally, Tuband, Reinhold and Jost /25/, found a relationship between the conductivity and the diffusion coefficient. Therefore, data on the electrolytic conductivity of salts can greatly supplement the results obtained from the study of diffusion of metals.

## § 1. Dependence of the rate of diffusion on the crystallographic directions (anisotropy of diffusion)

In a study on diffusion in single crystals of metals, the problem arises of the rate of diffusion in different crystallographic directions, and this has been little investigated. Therefore, the data available on the related phenomenon of the electrolytic conductivity of salts are of great interest.

The dependence of the electrolytic conductivity on the crystallographic directions of quartz was found by Joffe /26/. Recently, the dependence of electrolytic conductivity and self-diffusion on the crystallographic direction has been studied by Seith /27/. According to his earlier papers, the electrolytic conductivity of lead iodide can be written:

$$K = 9.78 \cdot 10^{-4} e^{-\frac{4680}{T}} + 1.15 \cdot 10^{-5} e^{-\frac{15000}{T}}.$$

The first term of the equation relates part of the electrical conductivity of iodide ions to the work of detachment equal to 9300 cal, and the second term relates the electrical conductivity of lead ions to the work of detachment equal to 30,000 cal. Seith cut samples from lead iodide single crystals perpendicular and parallel to the direction of the  $c$  axis of the crystal, and measured their conductivity at different temperatures over the range 270–380°C. These studies showed that the work of detachment in the direction parallel to the  $c$  axis is  $Q = 28,500$  cal, and in the direction perpendicular to the  $c$  axis it is  $Q = 8800$  cal. Thus, in the range of temperatures studied, the mobility of lead ions in the direction of the  $c$  axis is predominant, and determines the conductivity. On the other hand, in the direction perpendicular to the  $c$  axis the current is transported chiefly by iodide ions, and the mobility of lead becomes noticeable at elevated temperatures only.

These results indicate that there is a difference between the conductivity in various crystallographic directions because in certain directions the mobility of some ions is greater than the mobility of others. To confirm this, Seith studied the rate of self-diffusion of lead ions in the lattice of lead iodide, with ThB as a tracer. He found that the rate of self-diffusion is little influenced by direction. Seith explains the differences between the electrolytic conductivities in various directions as follows: lead iodide forms a laminated lattice in which a layer of lead atoms alternates between two layers of iodine atoms. To become detached from their sites, the lead ions need much more energy (30,000 cal) than the iodide ions (9000 cal). At a certain temperature the regions occupied by iodine atoms become greatly "loosened," and some atoms can interchange positions, but few lead atoms have sufficient energy for this. As a result, it is mainly iodide ions that interchange positions in the lattice, and since they are large they move chiefly in the direction of their layers, and only rarely penetrate between the ions of lead. Hence, the high mobility in the direction of the layer and the low mobility in the direction perpendicular to it. However, the small lead ions find their way in the direction of the  $c$  axis through the "loosened" iodine layers, as readily as directly toward neighboring lead atoms. Thus, the difference between the electrical conductivities is due to the presence of two types of ions in the lattice and not to the different mobilities of lead ions in different directions.



Seith also studied the self-diffusion of bismuth, with ThC as tracer. The bismuth lattice consists of two rhombohedrons placed one inside the other.

The main cleavage plane, which is the basis for hexagonal indexing, cuts through so that it contains only atoms of a single rhombohedron.

The rate of self-diffusion was measured in a direction parallel to this plane and in a direction perpendicular to it. The data are given in Figure 6, and show that the rate of diffusion in the direction of the  $c$  axis is very low. The diffusion coefficient at a temperature close to the melting point,  $D = 7 \cdot 10^{-11}$  cm<sup>2</sup>/day, is  $\frac{1}{10}$  of that in the direction perpendicular to the  $c$  axis (which coincides with the main cleavage plane). The temperature dependence of the diffusion coefficient in the direction of the  $c$  axis indicates a work (heat of loosening) of 31,000 cal, i.e., of the same order as for lead. This work is equal to 140,000 cal in the direction perpendicular to the  $c$  axis. The last value is very high, and even exceeds the heat of loosening during the diffusion of high-melting metals such as molybdenum and tungsten (35,000 cal). Seith explains the very high temperature coefficient of self-diffusion of bismuth as an anomaly of its thermal properties.

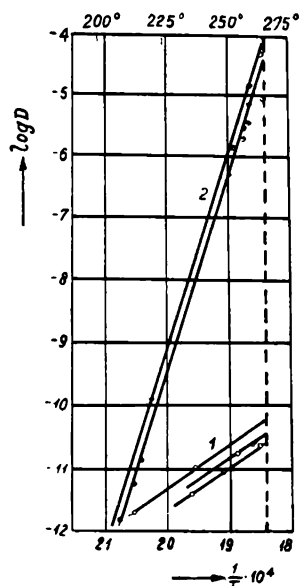


FIGURE 6. Coefficients of self-diffusion of bismuth according to Seith:

- 1—direction parallel to the  $c$  axis;
- 2—direction perpendicular to the  $c$  axis.

We believe that the increase in the difference between the diffusion rates in two directions perpendicular to one another with increase in temperature is also an anomaly. We should expect that an increase in temperature would increase the total loosening of the lattice, and

also the mobility of atoms, but that the anisotropy would decrease as the melting point is approached.

Thus, Seith's study does not solve the problem of the influence of the anisotropy of crystals on the diffusion rate and on the temperature dependence of the diffusion coefficient. However, this problem is of very great importance in studies on a number of problems, and in particular the mechanism of phase transformations in metals.

In metals with highly symmetrical crystal lattices, for example, with cubic lattices, we cannot expect any noticeable difference between the diffusion rates in different directions. Therefore, to study this problem it is preferable to use metals with less symmetrical lattices, for example, with hexagonal systems. Zinc, cadmium, and magnesium have such lattices.

We studied the anisotropy of diffusion in single crystals of zinc and cadmium [28/.

The first series of experiments included a qualitative study on the diffusion of mercury in single crystals of cadmium and zinc. The method was very simple. Single crystals of cadmium and zinc were grown by the usual method from a melt of pure starting materials, which had been distilled in vacuo. The orientation of the cadmium specimens (the position of the basal plane with reference to the axis of the specimen) was determined

by an optical method developed by Yakovlev. The orientation of the zinc specimens was found directly from the position of the cleavage plane. The single crystals were cut into several parts by etching, and a drop of mercury was put on the surface of each part. An amalgam was formed, and the mercury in contact with the metal surface rapidly solidified. Then the liquid mercury was removed. The specimens were heated to a given temperature, and metallographic sections were cut in a predetermined direction with reference to the axis of the sample. The paths of the diffusion of mercury in zinc and cadmium were examined at a small magnification. It was found that these paths are elliptical, and the slopes of their main axes depend on the orientation of the single crystal. Later experiments showed that the path formed a circle on the basal plane and not an ellipse which means that in this plane the diffusion proceeds at the same rate in all directions. On all other planes the paths were elliptic. Plate 1 (see Appendix) shows the paths of diffusion of mercury and cadmium on a basal plane and on a plane perpendicular to it. It is seen that the first is a circle and the second an ellipse.

Similar experiments at different temperatures can indicate the influence of temperature on the degree of the anisotropy of diffusion.

As a criterion, we took the ratio of the axes of the ellipse measured under a microscope at a small magnification.

The mean values are given in Table 18.

TABLE 18.

Diffusion of mercury in Cd		Diffusion of mercury in Zn	
Temperature, °C	Ratio of axes*	Temperature, °C	Ratio of axes*
50	0.70	50	0.68
100	0.72	100	0.73
150	0.75	150	0.79
200	0.89	—	—

\* Table 18 shows the ratio of the minor axis of the ellipse to the major, and therefore a decrease in this ratio indicates an increase in anisotropy.

The results show that: 1) there is anisotropy of diffusion, i. e., different rates of diffusion in different crystallographic directions, in metals of the hexagonal system (zinc, cadmium), but the difference is not great, as can be seen from the ratios of the axes of the ellipses, and 2) with increase in temperature the difference between the rates of diffusion along different axes decreases, and almost disappears near the melting point. This series of qualitative experiments established the existence of anisotropy.

We also studied the diffusion of copper in zinc single crystals. At the temperatures studied, a layer of a  $\gamma$ -phase containing 62—70% of zinc was formed. The mechanism of formation of intermediate phases, which are close to intermetallic compounds, is more complex than ordinary diffusion which involves the formation of a solid solution with a lattice of the solvent metal. However, the existence of diffusion anisotropy can also be determined qualitatively in this case, since the depth of the layers formed characterizes the rate of the process.

For studying the diffusion of copper in zinc the authors prepared zinc single crystals with square cross sections. The basal plane was exposed by cleaving the crystals in liquid air. The basal plane and the plane perpendicular to it were electrolytically coated with a 0.1 mm copper layer. To study the quality of the coating, a master specimen was prepared and examined under a microscope. It was found that the copper layer is uniform and adheres well to the surface of the crystal.

The copper plated specimens were heated in vacuo at 50, 100, 150, and 200°C for five days. The specimens were also heated at 150°C for one and three days.

For each operation we took four specimens, two for copper plating on the basal plane and two for plating on the plane perpendicular to it. After the specimens had been heated, metallographic sections were cut in planes perpendicular to the coated plane. Thus, when a zinc specimen was coated with copper on the basal plane, it was used to study the diffusion in the direction perpendicular to this plane, and if the copper was coated on the plane perpendicular to the basal plane, the diffusion was studied in the direction parallel to this. The thickness of the diffusion layer was measured under a microscope using an eyepiece micrometer calibrated against a master scale.

The diffusion layer produced at 50°C was so thin that it could not be measured. The mean results obtained in all other cases are given in Table 19.

TABLE 19.

$t$ °C	Duration of heating, days	Thickness of layer, mm	
		parallel to the basal plane	perpendicular to the basal plane
100	5	0.02	0.007
150	1	0.045	0.035
150	3	0.09	0.065
150	5	0.13	0.11
250	5	0.16	0.15

TABLE 20.

$t$ °C	Ratio of thicknesses of layers
100	0.4
150	0.84
200	0.9

Table 19 shows that the diffusion is more rapid in the direction parallel to the basal plane, and that a difference is noticeable below 200°C only. The layers produced at 250°C have almost the same thickness. Table 20 shows the ratio of the thicknesses of layers parallel and perpendicular to the basal plane measured at different temperatures.

Thus, the results for the diffusion of copper in zinc agree with those for the diffusion of mercury in zinc and in cadmium.

For a better quantitative study of the influence of anisotropy on the diffusion coefficient and on its temperature dependence, additional experiments were carried out on the diffusion of copper in zinc single crystals.

The method was based on the results of the diffusion of copper in zinc which we had already studied for other purposes.

These results show that the diffusion at relatively low temperatures (up to 250–300°C) produces a single intermediate  $\gamma$ -phase, which consists of the  $\text{Cu}_2\text{Zn}_5$  intermetallic compound. The diffusion layer has very well-marked boundaries which facilitate quantitative measurements.

We also found that the laws of diffusion for solid solutions hold also for the formation of intermediate phases, and thus the diffusion coefficient can be found.

As we shall later (see Part Two, page 83) the thickness  $y$  of the diffusion layer increases with increase in the time of diffusion  $t$  according to a parabolic law:  $y^2 = 2pt$ , where  $p$  is a quantity proportional to the diffusion coefficient, and differing from it by a constant factor only. By measuring the thickness of the diffusion layers formed in different crystallographic directions and with different times and temperatures of heating, diffusion coefficients in these directions and their temperature dependence can be determined.

The methods of measurement were the same as above. Basal planes of zinc single crystals and planes perpendicular to them were electrolytically coated with copper and heated at 100–250°C for different periods. For the microstructural analysis and measurements of the thickness  $y$  of the diffusion layers, a microscope was used with magnification 250. The measurements were correct within 0.5 mm (with a micrometer scale).

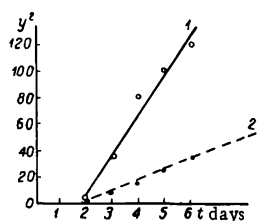


FIGURE 7. Diffusion of copper in zinc single crystals at 100°C:

- 1—parallel to basal plane;
- 2—perpendicular to basal plane.

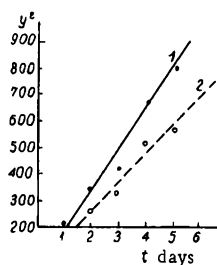


FIGURE 8. Diffusion of copper in zinc single crystals at 150°C:

- 1—parallel to basal plane;
- 2—perpendicular to basal plane.

The graph of  $y^2$  plotted against the diffusion time  $t$  is a straight line, and its slope gives the value of the parameter  $p$  of the parabola.

The results of the measurements are given in Tables 21—24 and in Figures 7—10.

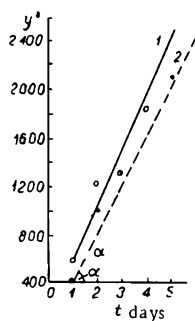


FIGURE 9. Diffusion of copper in zinc single crystals at 200°C:

1 — parallel to basal plane;  
2 — perpendicular to basal plane.

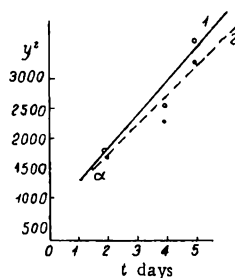


FIGURE 10. Diffusion of copper in zinc single crystals at 250°C.

1 — parallel to basal plane;  
2 — perpendicular to basal plane.

Since the absolute thicknesses are not important, the curves were plotted from values found directly by microscopic measurements (without multiplying by the microscope constant). Therefore, all values of the parameters  $p$  are  $(210)^2$  times the real value ( $7 \times 30 = 210$ , the magnification of the microscope). From the results the temperature dependence of the parameter  $p$  in the directions parallel and perpendicular to the basal plane were plotted (Table 25 and Figure 11).

Since the value of  $p$  differs from the diffusion coefficient by a constant factor only the curves representing the temperature dependence of  $p$  accurately reflect the temperature dependence of the diffusion coefficient.

These results indicate that the growth rate of the layers, and consequently the diffusion coefficient, are always higher in the direction parallel to the basal plane. The differences in the growth rates are especially great at low temperatures, and rapidly decrease with increase in temperature (Figure 11). The curves representing the temperature dependence of diffusion converge in the direction of high temperatures.

The heat of loosening  $Q$  can be determined from the curves representing the temperature dependence of the diffusion coefficients. It was found that in the direction parallel to the basal plane  $Q = 12,000$  cal, and in the direction perpendicular to the basal plane  $Q = 14,000$  cal.

The results of the above experiments can be summarized as follows:

1) we observed a diffusion anisotropy in single crystals of metals of the hexagonal system (cadmium and zinc). The rate of diffusion in the direction parallel to the basal plane (that is perpendicular to the hexagonal axis) is higher than that in the direction perpendicular to the basal plane.

TABLE 21. Diffusion of copper in zinc single crystals at 100°C

Direction of diffusion	Duration of heating, days	Mean thickness of layer $y \cdot 210$ mm	$y^2 \cdot (210)^2$ mm <sup>2</sup>
Parallel to basal plane ..	3	6	36
The same .....	4	9	81
" " .....	5	10	100
" " .....	6	11	121
Perpendicular to basal plane	3	3	9
The same .....	4	4	16
" " .....	5	4.5	20
" " .....	6	5	25

TABLE 22. Diffusion of copper in zinc single crystals at 150°C

Direction of diffusion	Duration of heating, days	Mean thickness of layer $y \cdot 210$ mm	$y^2 \cdot (210)^2$ mm <sup>2</sup>
Parallel to basal plane ..	2	18.5	372
The same .....	3	21	441
" " .....	4	26	676
" " .....	5	30	900
Perpendicular to basal plane	2	16	256
The same .....	3	18	324
" " .....	4	23	629
" " .....	5	24	576

TABLE 23. Diffusion of copper in zinc single crystals at 200°C

Direction of diffusion	Duration of heating, days	Mean thickness of layer $y \cdot 210$ mm	$y^2 \cdot (210)^2$ mm <sup>2</sup>
Parallel to basal plane ..	1	23	530
The same .....	2	35	1225
" " .....	3	39	1521
" " .....	4	43	1849
" " .....	5	49.5	2450
Perpendicular to basal plane	1	18	324
The same .....	2	32	1024
" " .....	3	—	—
" " .....	4	38	1414
" " .....	5	46	2116

TABLE 24. Diffusion of copper in zinc single crystals at 250°C

Direction of diffusion	Duration of heating, days	Mean thickness of layer $y \cdot 210$ mm	$y^2 \cdot (210)^2$ mm <sup>2</sup>
Parallel to basal plane ..	2	42	1764
The same .....	3	—	—
" " .....	4	52	2700
" " .....	5	60	3600
Perpendicular to basal plane	2	40	1600
The same .....	3	48	2304
" " .....	4	—	—
" " .....	5	56 — 58	3249

TABLE 25. Temperature dependence of the parameter  $\rho$  for the diffusion of copper in zinc single crystals

$t, ^\circ\text{C}$	$T_{\text{abs}}$	$\frac{1}{T} \cdot 10^3$	$\rho$		$\ln \rho$	
			parallel to basal plane	perpendicular to basal plane	parallel to basal plane	perpendicular to basal plane
100	373	2.7	20	5.0	3.0	1.60
150	423	2.3	200	110	5.30	4.61
200	473	2.1	460	400	6.10	5.99
250	523	1.9	585	550	6.37	6.30

2) the degree of anisotropy increases with decrease in the diffusion temperature. At elevated temperatures (for zinc 350—400°C) the diffusion coefficients are almost the same in both directions.

These results can apparently be explained by the fact that the atoms of mercury or copper, which have a relatively great volume, move more rapidly in those directions of the lattice which contain fewer atoms of the basis metal. In the lattices of zinc and cadmium these directions are parallel to the basal plane.

From the above we can conclude that there is no anisotropy of diffusion in crystals of the cubic system. We should like to add to our remarks at the beginning of this chapter and mention that Elam /29/ found that the diffusion of zinc in copper single crystals is the same in all directions. This has been confirmed by other authors. Mehl /30/ studied the diffusion of carbon in coarse-grained  $\gamma$ -Fe, and found the penetration into all the grains was the same, irrespective of their orientation. Similar results were obtained by other authors.

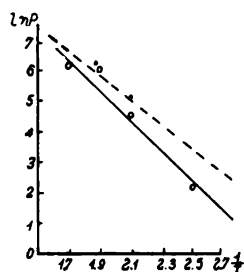


FIGURE 11. Temperature coefficient of diffusion of copper in zinc single crystals.

## § 2. Diffusion and defects in the crystal structures of metals

The structure of real crystals differs from that expected according to the type of their crystal lattices.

This is due mainly to the conditions of crystal growth.

The influence of the crystal defects on the diffusion rate has not yet been sufficiently studied and it is still a controversial subject. There are very few experimental studies in this field.

The most important aspects of this problem will be discussed below.

a) **Ideal and real crystals.** An ideal crystal is one with a geometrically perfect lattice.

When real crystals are examined under a microscope, it is seen that they differ from ideal crystals since they contain small nonuniform regions with irregular crystal lattices.

Irregular structures occur because of the conditions of crystal growth, and the presence of impurities in real crystals. Irregularities in the distribution of atoms occur mainly in the surface layers of the crystals.

The distance between the external crystal plane and its neighboring plane is a few percent less than the distances between the internal planes of the crystal. This shortening is due mainly to the one-sided deformation of the surface atoms, and it is restricted to the upper layer of the lattice. A change in the forces of interaction in the surface layers can lead to a number of secondary effects, such as the disturbance of the thermal vibrations in the lattice, a change in the field of force of the atom, etc.

Besides the irregularities in the distribution of atoms on the surface of crystals, there can be heterogeneities and distortions in the interior of the crystal lattice.

We can imagine that uniformly distributed loosening sites of microscopic dimensions can be formed as a result of thermal motion, but greater distortions in the lattice take place during crystallization.

The lattice distortions formed as the result of interstitial atoms are of particular interest in the study of diffusion. For close-packed lattices in which the lattice constant is calculated as the sum of atomic radii, for geometrical reasons it is difficult to assume that interstitial atoms exist. On the other hand, in solid solutions with atoms of the solute located in the interstices of the lattice (for example, in a solution of carbon in iron, hydrogen in palladium, etc.), we can imagine that atoms of the solvent can also assume a similar position.

The concept of ideal and real crystals is related to that of "structurally sensitive" and "structurally insensitive" properties of crystals, and with the phenomena taking place in them. If two specimens of the same crystalline substance are prepared separately and give values which differ by more than the experimental error, the properties can be considered as "structurally sensitive." If, however, the differences are small, and lie within the experimental error, then the properties are "structurally insensitive." The dependence of the properties on the crystal structure of the substance is related to nonuniform structures found in real crystals, which are mainly due to the conditions of crystallization and the presence of impurities.

Trace amounts of impurities, which are impossible to determine by any method of analysis ( $10^{-6}$ — $10^{-8}\%$ ) can appreciably influence the properties of crystals. Therefore, these impurities form an almost nonremovable factor which produces a structural sensitivity of the properties of crystals and of the phenomena taking place in them.

The structurally sensitive properties and phenomena common to all crystalline substances are mechanical properties, diffusion, and electrolytic conductivity [31].

### § 3. Influence of the grain size on the diffusion coefficient

The role of the "internal planes" in real crystals has not yet been sufficiently clarified, but the influence of external facets of polycrystalline



aggregates on diffusion is better known. Usually, the formation of new, free facets involves an increase in the mobility of the atoms. This is confirmed by the results of a number of studies on the ionic conductivity of salts and the diffusion of metals.

Joffe and Zechnowitzer /35/ studied the variation in electrolytic conductivity during plastic deformation of common salt, and found that the electrolytic conductivity changes only when a new, free shear plane is formed.

Tammann and Veszi /36/, and Hevesy carried out similar studies, and found that polycrystalline specimens have a higher electrolytic conductivity than single crystals.\*

Similarly, it has often been noticed that the diffusion rate increases if the surface area of the grain boundaries is increased in the polycrystalline aggregate. Thus, van Liempt /37/ found that at 1600°C the rate of diffusion of molybdenum in a polycrystalline aggregate of tungsten (with an average grain size of  $20\mu$ ) is ten times that in a single crystal of tungsten. Zwikker /38/ found that the rate of diffusion of carbon in fine-grained tungsten is four times that in tungsten single crystals. Rhines /30/ showed by experiment that the rate of diffusion of copper in zinc single crystals is  $\frac{1}{6}$  of that in polycrystalline zinc. A similar influence of the grain size on the rate of diffusion was found by other authors /39, 40, 41/.

All these studies indicate that the absolute value of the diffusion coefficient increases with increase in the surface area of the grain boundaries, that is with decrease in the grain size.

It would be interesting to find the influence of the grain size on the absolute values of the diffusion coefficients and on their temperature dependence, and therefore on the heat of loosening  $Q$ . This problem has so far been little studied.

According to van Liempt, the value of  $Q$  for the diffusion of molybdenum in tungsten is the same for single crystals and for polycrystalline aggregates ( $Q = 40,290$ ), despite the fact that the absolute values of the diffusion coefficients are appreciably higher in the first case. Foneta, Jound, and Walker /42/ studied the diffusion of thorium in a wire of tungsten of various grain sizes ( $5.3\mu$ ,  $7.3\mu$  and  $3000\mu$ ), and found that the temperature curves of the diffusion coefficient are always parallel. Langmuir, however, determined that in this case the heat of loosening is greater for diffusion in the interior of the grain than along the grain boundaries ( $Q = 120,000$  cal/mole and  $Q = 90,000$  cal/mole, respectively).

To obtain additional data on the still unsolved question of the diffusion coefficients in single crystals and in polycrystalline specimens of various grain sizes, and to check the above results obtained for other metals, we /43/ determined the diffusion coefficient of zinc in copper single crystals and in polycrystalline brass samples of various grain sizes.

The coefficient was found by evaporating zinc from brass. Brass specimens of known grain size were heated in vacuo ( $10^{-1}$  mm Hg) at a given temperature, and the amount of evaporated zinc was determined every 30 minutes. By plotting the time  $t$  on the abscissa and the value of

$\ln \frac{dQ}{dt}$  on the ordinate, we obtained a straight line inclined at an angle  $\alpha$  to the axis  $t$ . This can be used to determine the diffusion coefficient from the

\* The results of these authors will be discussed later.

Grinberg formula /44/

$$\operatorname{tg} \alpha = \frac{5.78D}{r^2},$$

where  $r$  is the radius of the specimen. Thus, we were able to find the diffusion coefficient  $D$  for each grain size and at each of the temperatures studied.

Our starting material was brass, which had been melted out from electrolytic copper and (Kalbaum) zinc. The alloy contained 30% of zinc, and was drawn into a 2 mm-diam wire. Specimens 15 mm long and 1–1.5 mm in diameter were prepared from this wire. The differences in grain size were achieved by cold working the metal to different degrees of reduction, and recrystallizing. The recrystallization temperature was always higher than the highest diffusion temperature, otherwise the grain would continue to grow during diffusion.

Brass single crystals were also prepared by recrystallizing metal which had been deformed to a 2.5% reduction. In this case the temperature of recrystallization was close to the melting point. The required diameter of the specimen (1–1.5 mm) was obtained by etching the surface in dilute nitric acid.

To determine the diffusion coefficient the specimens were weighed on microanalytical balances, correct to within 0.00005 g. The grain size was determined under a microscope as the mean value of 40–50 measurements (correct to within 0.02 mm).

We also measured the diffusion coefficient  $D$  in single crystals and in polycrystalline specimens with a grain size of 0.13, 0.37, and 0.48 mm. We found the diffusion coefficients by means of curves representing the weight loss of specimens plotted in  $\ln \frac{dQ}{dt} - t$  coordinates. The coefficients are given in Tables 26–29 (for from 700 to 900°C), and are also plotted in  $\ln D$ ,  $1/T$  coordinates in Figure 12.

TABLE 26. Grain size 0.13 mm

$t^\circ \text{C}$	$\frac{1}{T_{\text{abs}}} \cdot 10^4$	$D \text{ cm}^2/\text{day}$	$\ln D$
850	8.9	$8.5 \cdot 10^{-2}$	— 2.46
800	9.3	$4.8 \cdot 10^{-2}$	— 3.03
750	9.7	$3.2 \cdot 10^{-2}$	— 3.22
700	10.3	$2.3 \cdot 10^{-2}$	— 3.67

TABLE 27. Grain size 0.37 mm

$t^\circ \text{C}$	$\frac{1}{T_{\text{abs}}} \cdot 10^{-4}$	$D \text{ cm}^2/\text{day}$	$\ln D$
900	8.5	$2.74 \cdot 10^{-2}$	— 3.59
800	9.3	$1.11 \cdot 10^{-2}$	— 4.51
750	9.7	$0.83 \cdot 10^{-2}$	— 4.83
700	10.3	$0.78 \cdot 10^{-2}$	— 4.85

TABLE 28. Grain size 0.48 mm

$t^{\circ}\text{C}$	$\frac{1}{T_{\text{abs}}} \cdot 10^4$	$D \text{ cm}^2/\text{day}$	$\ln D$
900	8.5	$2.3 \cdot 10^{-2}$	-3.77
850	8.9	$1.1 \cdot 10^{-2}$	-4.51
800	9.3	$1.4 \cdot 10^{-3}$	-4.25
750	9.7	$0.55 \cdot 10^{-3}$	-5.22
700	10.3	$0.40 \cdot 10^{-3}$	-5.52

TABLE 29. Single crystal

$t^{\circ}\text{C}$	$\frac{1}{T_{\text{abs}}} \cdot 10^4$	$D \text{ cm}^2/\text{day}$	$\ln D$
900	8.5	$0.37 \cdot 10^{-2}$	-5.52
800	9.3	$0.22 \cdot 10^{-2}$	-6.21
750	9.7	$0.07 \cdot 10^{-2}$	-7.24
700	10.3	$0.06 \cdot 10^{-2}$	-7.41

Figure 12 shows that a decrease in the grain size leads to a rapid increase in the diffusion coefficient. The differences between the diffusion coefficients in single crystals and in polycrystalline specimens are particularly great.

Thus, at  $700^{\circ}\text{C}$ ,  $D = 0.06 \cdot 10^{-2} \text{ cm}^2/\text{day}$  for single crystals and  $D = 2.3 \cdot 10^{-2}$  for a specimen with a 0.13 mm grain size (i.e., a forty-fold increase). As the temperature is increased, these differences become smaller.

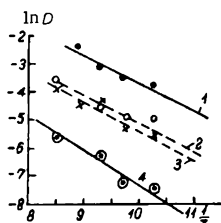
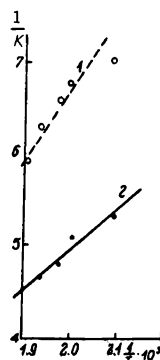


FIGURE 12. Dependence of the diffusion coefficient on the grain size:

1—0.13 mm; 2—0.37 mm; 3—0.48 mm; 4—single crystal.

FIGURE 13. Electrical resistivity of  $\text{NaNO}_3$  according to Hevesy:

1—single crystal; 2—polycrystalline aggregate.

The temperature dependence of the diffusion coefficient is almost uninfluenced by the grain size in polycrystalline specimens, and the straight lines are almost parallel. Thus, the data of Foneta, Jound, and Walker are

confirmed. In the diffusion of thorium in tungsten, the temperature dependence of the diffusion coefficient in polycrystalline aggregates is different from that in single crystals. The heat of loosening calculated from the temperature curves is  $Q = 20,000$  for polycrystalline specimens of all grain sizes, and  $Q = 25,000$  for single crystals, which means that the energy required for the interchange of the position of atoms is about 25% higher in single crystals than in polycrystalline aggregates.

Our results differ somewhat from those of van Liempt /37/, who found that the heat of loosening  $Q$  is the same for single crystals as for polycrystalline specimens.

Nevertheless, certain indications, especially the experimental data on the electrolytic conductivity of salts, confirm the correctness of our conclusions.

Comparative studies on the electrolytic conductivity of salts in single crystals and in polycrystalline specimens were carried out by Hevesy and by Tammann and Veszi. The results are very similar to ours on diffusion in copper.

Figure 13 shows the temperature dependence of the electrical resistivity of single crystals and of polycrystalline specimens plotted from the data of Hevesy /45/. As in our studies the slope of the temperature curve which determines the value of the heat of loosening  $Q$  is appreciably greater for single crystals than for polycrystalline specimens. Similar results were obtained by Tammann and Veszi in their investigation of the electrolytic conductivity of a number of salts. From the results for potassium chloride, these authors calculated the difference between the electrolytic conductivity in the interior of the crystal and on its surface. They found that  $\frac{K_b}{K_{in}} = 3 \cdot 10^2 - 150 \cdot 10^2$ , i. e., the electrolytic conductivity in the boundary layers is 300—15,000 times greater than in the interior of the crystal. It is interesting that the electrolytic conductivity of fused KCl is  $10^4$  times that of a single crystal at the melting point.

Thus, these calculations show that the energy state of atoms on the grain boundaries is close to that in liquids.

Tammann and Veszi believe that the reasons why the mobility of atoms is considerably higher in polycrystalline specimens than in single crystals are as follows:

- 1) single crystals have a fixed crystallographic direction (unlike polycrystalline aggregates);
- 2) in single crystals the impurities are distributed differently than in polycrystalline aggregates.

It has been found that in metals with a cubic lattice the different crystallographic orientations of single crystals and of polycrystalline substances cannot be the reason for the higher electrolytic conductivity or the higher intensity of diffusion in polycrystalline aggregates.

Studies on the influence of impurities on the mobility of particles in polycrystalline substances must be based chiefly on measurements of the electrolytic conductivity since there have been no systematic investigations on the diffusion of metals. The influence of impurities on the electrolytic conductivity is considerable, but it is different for single crystals and for polycrystalline aggregates. In single crystals impurities enter the solid solution, and in polycrystalline aggregates they concentrate on the grain boundaries. The influence of impurities on the electrolytic conductivity

of a polycrystalline substance should therefore be greater than that on the conductivity of single crystals.

However, Tamman and Veszi found that the removal of impurities has the same effect on the electrolytic conductivity of both single crystals and polycrystalline substances.

In any case, the considerable increase in the mobility of atoms at the grain boundaries cannot be explained by the above reasons.

To explain this, we should start with the Hevesy theory on the greater loosening of intercrystalline layers. The fairly large amount of experimental data on the nature and properties of intercrystalline layers show that the structure of these layers differs from that of the crystal since these layers contain irregularly located atoms. As a result, the binding forces between the atoms are smaller, and to detach such atoms from their equilibrium position less energy is needed than for the detachment of atoms in crystals. Obviously, even a small difference in the heat of loosening (about 20% in our case) can lead to a considerable increase in the diffusion coefficient of polycrystalline substances.

Apparently, small differences between the heat of loosening of single crystals and of polycrystalline substances should always be expected, otherwise it would be impossible to explain the considerable differences in the absolute values of the diffusion coefficients.\* It can be seen that a decrease in the grain size of polycrystalline substances has no influence on the value of  $Q$  because the energy state of the atoms in the intercrystalline layers is not changed by this decrease, and only the relative surface occupied by the grain boundaries increases.

If we consider the differences between the values of  $Q$  for crystals and intercrystalline layers, we cannot state that the temperature dependence of the diffusion coefficient for polycrystalline specimens is governed by an exponential law. However,  $D$  can be written as the sum of exponents:

$$D = A_{in} e^{-\frac{Q_{in}}{RT}} + A_b e^{-\frac{Q_b}{RT}}.$$

If the difference between  $Q_{in}$  and  $Q_b$  is small, then the deviation from the exponential law is almost negligible.

Our study on the influence of the grain size on the diffusion process was based on experimental data, which usually indicate that the diffusion coefficient increases with decrease in the grain size.

However, some authors state that the diffusion rate is not influenced by the grain size. Thus, Seith and Keil /46/ were unable to find any relationship between the grain size and the coefficient of self-diffusion of lead. Elam /29/ studied the diffusion of zinc in copper, and found no preferable penetration of zinc along the grain boundaries of copper crystals. Similar results were obtained by Rhines /30/. It was found that the grain boundaries exerted no influence on the diffusion of carbon in  $\gamma$ -Fe and in  $\alpha$ -Fe.\*\*

\* In fact, if we consider that  $Q$  varies, the increase in  $D$  for polycrystalline specimens can be explained only by the increase in the interatomic distances in the intercrystalline layers, and as is known, this cannot have any great influence.

\*\* According to Andreev, Kontorovich, and Savelova /47/ grain coarsening of "Armco" iron even increases the depth of diffusion of nitrogen. In fine-grained iron the depth of penetration of nitrogen is 0.26 mm, and in coarse-grained it is up to 0.58 mm. Kontorovich also found that grain coarsening increases the rate of diffusion of carbon in titanium and in steel. The authors assume that the formation of interstitial solid solutions in more energetically stable systems increases the diffusion rate.

These data, though few, indicate that the influence of the external surfaces of crystals is not general. However, these exceptions cannot influence our earlier conclusions, and they are even understandable if we consider that the influence of the external surfaces is related to the "structural" sensitivity of diffusion in various metals.

The grain boundaries must be identified with internal crystal defects, and their role considered as that of these defects.

We have already mentioned that the importance of crystal imperfections can vary. For example, they can only slightly influence the self-diffusion of metals, including lead. We can thus explain the results of Seith and Keil, who found that the grain boundaries had no influence on the rate of self-diffusion of lead. Similarly, it can be assumed that the grain boundaries will have little influence on the self-diffusion of other metals.

## Chapter IV

### DEPENDENCE OF THE DIFFUSION COEFFICIENT ON THE CONCENTRATION OF IMPURITIES

The diffusion coefficient can be found from experimentally determined concentrations of impurities by means of the following formula:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \quad (1)$$

Formula (1) is correct only if  $D$  does not depend on  $x$ . If the solvent metal is homogeneous, and the temperature is always the same, the dependence of  $D$  on  $x$  is tantamount to the dependence of  $D$  on the concentration of impurities. However,  $D$  remains independent of the concentration of impurities over a narrow range of concentrations only, particularly during diffusion in a solid metal. This must be taken into account when determining the absolute values of the diffusion coefficient from experimental data.

If  $D$  does depend on concentration, then instead of equation (1) we must use a more general equation obtained as follows. From the continuity equation for diffusing metals it follows that

$$\frac{\partial c}{\partial t} = -\operatorname{div} j,$$

where  $j$  is the flux density. Assuming that  $j = -D \operatorname{grad} c$ , we obtain

$$\frac{\partial c}{\partial t} = \operatorname{div} (D \operatorname{grad} c). \quad (2)$$

If the concentration depends on a single coordinate  $x$  only, then formula (2) can be written as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right). \quad (3)$$

Since  $D$  depends on  $c$ , it also depends on  $x$ , and therefore  $D$  must not be taken out of the sign of the derivative. Matano /48/ suggested a method for determining  $D$  from experimental data when  $D$  depends on  $c$ . This method is based on the experimentally found relationship between the distance  $x$  from the boundary plane to the point at which the concentration is measured and the diffusion time  $\tau$ . This relationship can be written:

$$x = \lambda \sqrt{\tau},$$

where  $\lambda$  depends on concentration only. It has been calculated that

$$D = -\frac{1}{2} \frac{d\lambda}{dc} \int_0^c \lambda dc,$$

if  $\int_0^1 \lambda dc = 0.$

From formula  $x = \lambda\sqrt{t}$ , we can write the formula for  $D$  as follows:

$$D = -\frac{1}{2t} \frac{dx}{dc} \int_0^c x dc, \quad (4)$$

provided that

$$\int_0^1 x dc = 0.$$

Mehl and Rhines /22/ used formula (4) for a graphical determination of the diffusion coefficient. They obtained an ordinary diffusion curve experimentally in  $x, c$  coordinates, where  $x$  is the distance from the boundary planes, and  $c$  is the concentration of the diffusing substance. The value of  $\frac{dx}{dc}$  was found from the slope of the tangent to the curve at the point corresponding to a given concentration. The value of  $\int_0^c x dc$  was determined as the area included between the section of the diffusion curve in the range of concentrations from 0 to  $c$ , and the line corresponding to the interface. Figure 14 shows Mehl's diagram for determining the diffusion coefficient of aluminum in copper.

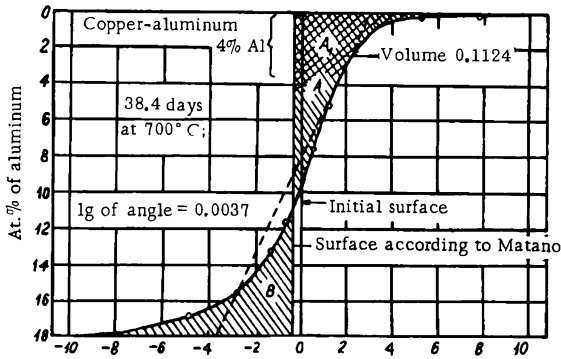


FIGURE 14. Determination of  $D$  according to Mantano and Mehl.



This diagram gives as an example the method for determining  $D$  at a concentration of 4% of aluminum. The double hatched surface corresponds to the value  $\int_0^{0.04} x \, dc$ . The broken line represents the slope of the curve at the point corresponding to the above concentration.

The method suggested by Matano and further improved by Mehl and Rhines is applicable only if we have a complete concentration—depth of penetration curve, which is difficult to plot experimentally.

The influence of the concentration of impurities is interesting not only to find accurate diffusion coefficients, but also because it indicates how the nature of the solid solution formed as a result of diffusion differs from that of ideal solutions. It is therefore important to determine the concentration of the impurity metal at which  $D$  is not yet influenced by its concentration.

The influence of concentration on the heat of loosening is of particular interest. Therefore, as in other cases, we must study not only the absolute values of the diffusion coefficient  $D$ , but also its temperature dependence.

Dunn /49/ was one of the first to study this field. He found the temperature dependence of the coefficient of diffusion of zinc in  $\alpha$ -brass (initial content of zinc 9.58% and 29.08%), and noted that the absolute value of the diffusion coefficient increases with increase in the concentration of zinc, but the temperature dependence of the diffusion coefficient (and consequently the  $Q$  value), remains unchanged.

Seith and Keil /50/ studied the results of Dunn, and concluded that the differences between the diffusion coefficients at different concentrations are due to the different melting points of the alloys only. In other words, the concentration of impurities as such has no influence.

To clarify the influence of the concentration of impurities on the diffusion coefficient we studied /51/ the diffusion of cadmium and of zinc in silver at different concentrations of the diffusing metals. As starting materials we took silver (Kalbaum) and zinc and cadmium (A.P.). The zinc and cadmium were also preliminarily distilled in vacuo to obtain a material of maximum purity. The diffusion coefficients were determined by the method of evaporation. The initial (maximum) concentration of the diffusing metal was 5, 10, and 15 wt % of cadmium in silver, and 5, 10, and 15 wt % of zinc in silver, which corresponds to 4.8, 9.6, and 14.5 at. % of cadmium in silver, and 8.2, 16.4, and 24.6 at. % of zinc in silver. The composition of these alloys was determined by chemical analysis to within 0.2—0.5 wt %. The samples were prepared in the form of cylinders 0.5 mm in diameter, which were then rolled and drawn into wire with a diameter which varied from 0.7 to 0.45 mm, depending on the diffusion temperature. The wire was cut into specimens 2 cm long, and these were heated in vacuo to different temperatures over the range 700—900°C. The specimens were taken out of the furnace after the same periods of time, and their weight loss  $\Delta q / \Delta t$  was determined to within 0.00002 g. From these data, curves were plotted in  $\Delta q / \Delta t$  (or  $\Delta q$ , since  $\Delta t$  was constant) and  $t$  coordinates. The values of  $D$  were determined from the slope  $\alpha$ . Some of the data from the study of the diffusion of cadmium in silver and of zinc in silver at different concentrations of the diffusing metal are given in Tables 30—36. The temperature curves  $\ln D - \frac{1}{T}$  are given in Figures 15—20.

TABLE 30. Ag-Cd (5% Cd)

$T^{\circ}\text{K}$	$\frac{1}{T^{\circ}} \cdot 10^4$	$D \cdot 10^2$ $\text{cm}^2/\text{day}$	$\ln D$
1173	8.5	0.054	-7.52
1123	8.9	0.035	-7.96
1073	9.3	0.011	-9.11

TABLE 31. Ag-Cd (10% Cd)

$T^{\circ}\text{K}$	$\frac{1}{T^{\circ}} \cdot 10^4$	$D \cdot 10^2$ $\text{cm}^2/\text{day}$	$\ln D$
1123	8.8	0.21	-6.16
1073	9.3	0.20	-6.21
1023	9.8	0.09	-7.01
973	10.3	0.05	-7.59

TABLE 32. Ag-Cd (15% Cd)

$T^{\circ}\text{K}$	$\frac{1}{T^{\circ}} \cdot 10^4$	$D \cdot 10^2$ $\text{cm}^2/\text{day}$	$\ln D$
1123	8.9	0.15	-6.49
1073	9.3	0.11	-6.81
1023	9.8	0.13	-6.65
973	9.8	0.13	-6.90

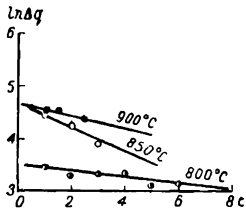


FIGURE 15. Diffusion of Cd in Ag (5% Cd).

$T^{\circ}\text{C}$	$\text{tg } \alpha$	$D \cdot 10^{-2}$	$d$ mm
900	0.11	0.054	0.7
850	0.22	0.035	0.45
800	0.07	0.011	0.45

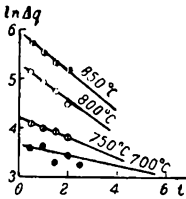


FIGURE 16. Diffusion of Cd in Ag (10% Cd).

$T^{\circ}\text{C}$	$\text{tg } \alpha$	$D \cdot 10^{-2}$	$d$ mm
850	0.42	0.21	0.7
800	0.40	0.20	0.7
750	0.19	0.09	0.7
700	0.10	0.05	0.7

The lowest concentration of the diffusing substance in our experiments was 5%, since the conditions of these experiments made it difficult to determine the diffusion coefficients at lower concentrations. Therefore, to determine  $D$  at very low concentrations of diffusing metals in Ag—Cd systems, we used the data of Seith et. al., /19/, who studied the diffusion of different metals in silver at very low concentrations of the diffusing metal. In the diffusion of cadmium in silver, the concentration of cadmium did not exceed 0.3%. By comparing the coefficients of diffusion of cadmium in silver obtained by Seith et. al., with our values for 5 wt% Cd (4.8 at. % Cd), it was possible to determine whether the diffusion coefficient changes over the range 0—5% of cadmium.

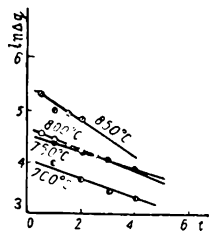


FIGURE 17. Diffusion of Zn in Ag (5% Zn).

$T^{\circ} \text{C}$	$\lg a$	$D \cdot 10^{-2}$	$d \text{ mm}$
850	0.35	0.10	0.520
800	0.21	0.06	0.52
750	0.17	0.04	0.50
700	0.16	0.04	0.50

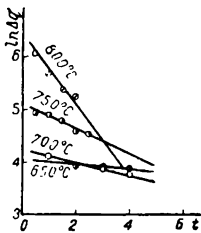


FIGURE 18. Diffusion of Zn in Ag (15% Zn).

$T^{\circ} \text{C}$	$\lg a$	$D \cdot 10^{-2}$	$d \text{ mm}$
800	0.69	0.34	0.7
750	0.22	0.11	0.7
700	0.13	0.05	0.65
650	0.08	0.03	0.65

TABLE 33. Diffusion of Cd in Ag

Temperature $^{\circ} \text{C}$	Diffusion coefficient at a concentration of 5% Cd, $\text{cm}^2/\text{day}$	Diffusion coefficient according to Seith et al.
900	$5.4 \cdot 10^{-4}$	$11 \cdot 10^{-4}$
850	$3.5 \cdot 10^{-4}$	$4.1 \cdot 10^{-5}$
800	$1.1 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$

TABLE 34. Ag - Zn (5% Zn)

$T^{\circ}\text{K}$	$\frac{1}{T^{\circ}} \cdot 10^4$	$D \cdot 10^2$ $\text{cm}^2/\text{day}$	$\ln D$
1123	8.9	0.10	-6.90
1073	9.3	0.06	-7.41
1023	9.8	0.04	-7.82
987	10.3	0.04	-7.82

TABLE 35. Ag - Zn (10% Zn)

$T^{\circ}\text{K}$	$\frac{1}{T^{\circ}} \cdot 10^4$	$D \cdot 10^3$ $\text{cm}^2/\text{day}$	$\ln D$
1123	8.9	0.20	-6.21
1073	9.3	0.08	-7.13
1023	9.8	0.06	-7.41
973	10.3	0.04	-7.82

TABLE 36. Ag - Zn (15% Zn)

$T^{\circ}\text{K}$	$\frac{1}{T^{\circ}} \cdot 10^4$	$D \cdot 10^2$ $\text{cm}^2/\text{day}$	$\ln D$
1073	9.3	0.34	-5.68
1023	9.8	0.11	-6.81
973	10.3	0.05	-7.59
923	10.8	0.03	-8.10

Table 33 shows that the data of Seith et al., for very low concentrations of the diffusing substance agree well with our data obtained for 5% Cd, particularly at 800°C. This indicates that in the range 0 – 5% of cadmium, the diffusion coefficient  $D$  remains approximately constant (within the experimental error), and consequently the fundamental equation for diffusion holds for this concentration range also.

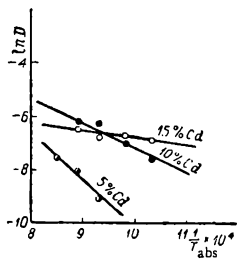


FIGURE 19. Diffusion of Cd in Ag.

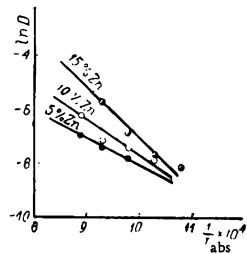


FIGURE 20. Diffusion of Zn in Ag.

Tables 30—33 show that for 10 wt % of cadmium the values of  $D$  are very different from those for 5% of cadmium. This difference increases with decrease in temperature. At 800°C,  $D_{10\%}$  is 20 times  $D_{5\%}$ . Thus, the values of  $D$  determined at an initial concentration of 10% of cadmium are not the real diffusion coefficients.

With 15% of cadmium the value of  $D$  is not very much smaller than  $D_{10\%}$ , but as the temperature decreases,  $D_{10\%} - D_{15\%}$  increases.

Although it was impossible to determine whether the diffusion coefficient of zinc in silver in the range 0—5 wt % of zinc changes, Tables 34—35 indicate that the differences between the diffusion coefficients for 5 and 10 wt % of zinc (or 8 and 16 at. % of zinc) are small. Therefore, for concentrations in the range 0—5% of zinc, the difference should also be small.

It should be pointed out that the differences between the diffusion coefficients for various concentrations of zinc in silver are more or less noticeable at elevated temperatures only, and decrease greatly as the temperature decreases. At 700°C,  $D$  is almost the same for all concentrations of the diffusing metal. The opposite occurs during the diffusion of cadmium in silver.

During the diffusion of cadmium in silver the heat of loosening decreases with increase in the concentration of cadmium, but during the diffusion of zinc in silver the heat of loosening increases. This last result is somewhat unexpected, since it seems probable that as the concentration of the diffusing metal increases, the lattice of the solvent becomes more loosened, which should lead to a decrease in the value of  $Q$ .

The above data, however, are insufficient for determining the relationship between the heat of loosening and the concentration of the diffusing metal. The results of these experiments only indicate that the temperature dependence of the diffusion coefficient varies with variation in the concentration of the diffusing metal, and therefore the above conclusions of Seith are not confirmed.

We found by experiment that the concentration influences the diffusion of cadmium in silver more than that of zinc in silver, because the atomic volume of cadmium is larger than that of zinc.

The present study was soon followed by the thorough research of Mehl and Rhines /22/ on the diffusion of zinc, aluminum, beryllium, cadmium, silicon, and tin in copper. Their results confirm our conclusions on the different influences of the concentration on the temperature dependence of the diffusion coefficient.

Thus, Mehl and Rhines found that an increase in the concentration of zinc and tin in copper decreases the value of  $Q$ , but an increase in the concentration of beryllium, silicon, and aluminum has the opposite effect. Thus, the nature of the variation in  $Q$  with concentration apparently depends on the nature of the diffusing metal.

The chief conclusion of Mehl and Rhines was that for low concentrations the coefficients of diffusion of different metals in copper are close to one another and become even closer as the concentrations approach zero. They thus concluded that with extrapolation to a zero concentration the diffusion coefficient of any metal becomes equal to the coefficient of self-diffusion of the solvent metal, and the coefficient of self-diffusion of the basis metal can be determined from the concentration—diffusion coefficient curve. This

conclusion is somewhat erroneous, since the authors extend their theory on the equality of the diffusion coefficients at low concentrations (at zero concentration) to any temperature.

Their own curves indicate that the diffusion coefficients referred to zero concentration ( $D_c \rightarrow 0$ ) can be considered approximately equal at elevated temperatures only, close to the melting point of copper. If the temperature is decreased, the difference between the values of  $D$  increases.

The curves of Mehl and Rhines confirm our conclusion on the diffusion of gold and silver in lead, namely: curves showing the temperature dependence of the diffusion of different metals in the same solvent intersect at approximately the same temperature close to the melting point of the solvent metal. This is true, in particular, for high-melting metals.

To a certain approximation it can also be said that the curve representing the self-diffusion of the basis metal intersects at the same point. Therefore, the method of Mehl and Rhines can be used to find the coefficient of self-diffusion of copper at a temperature close to its melting point only.

Mehl and Rhines believe that the heat of loosening  $Q$  is almost the same for different metals at concentrations close to zero. But this conclusion has not been proved.

According to the same authors, when the values of  $Q$  for different diffusing metals are extrapolated to  $c=0$ , they differ from one another. For example, for the diffusion of beryllium in copper  $Q=28,000$  cal, for the diffusion of tin in copper,  $Q=45,000$  cal, and for the self-diffusion of copper  $Q=57,200$  cal. The last value was found by Steigman and co-workers.

Since the conclusions of Mehl and Rhines contradict the data of Seith and co-workers on diffusion in lead and silver, and their main conclusion on the dependence of the diffusion rate on the relative positions of the solute and solvent metals in the periodic table, Seith and Herrmann /52/ recently studied the influence of the concentration of the impurities on the diffusion coefficient. To confirm their point of view, Seith and Herrmann accurately measured the diffusion coefficients of magnesium and thallium in lead at different concentrations of the diffusing metal. Their results show that during the diffusion of magnesium in lead at  $250-270^\circ\text{C}$ , the diffusion coefficient increases from  $5 \cdot 10^{-5}$  cm<sup>2</sup>/day to  $9 \cdot 10^{-5}$  cm<sup>2</sup>/day when the concentration of the diffusing metal is increased from 0.5 to 3.5 at. %. However, extrapolation to a zero concentration gives a value appreciably greater than that of the self-diffusion of lead. Thus, at  $245^\circ\text{C}$  and  $c=0$ ,  $D$  is about  $4 \cdot 10^{-5}$  cm<sup>2</sup>/day, but the coefficient of self-diffusion of lead at the same temperature is only  $9 \cdot 10^{-7}$  cm<sup>2</sup>/day.

A study of the diffusion of thallium and lead at concentrations from 8.5 to 53 at. % showed that the concentration has no influence on the diffusion coefficient. As in Seith's previous work,  $A=9 \cdot 10^{-4}$  cm<sup>2</sup>/day and  $Q=24,600$  cal.

Seith and Hermann also found that it is impossible to determine the coefficient of self-diffusion at any temperature by extrapolating the  $D$ -composition curve, and that sometimes the diffusion coefficient is not influenced by the concentration of the diffusing metal.

From our experimental data and those of other authors, the following conclusions can be drawn on the influence of the concentration of the diffusing metal on its diffusion coefficient and on the heat of loosening.

- 1). The diffusion coefficient is usually influenced by the concentration of the diffusing metal, and decreases with increase in this concentration.

However, sometimes as in the diffusion of thallium in lead, the concentration of the diffusing metal has no influence on the diffusion coefficient. \*

The influence of the concentration of the diffusing metal on the diffusion coefficient depends on the nature of the metal.

2). At very low concentrations of the diffusing metal (close to zero), the diffusion coefficient is still appreciably higher than the coefficient of self-diffusion of the solvent metal. But at temperatures close to the melting point of the solvent metal these values become comparable, so that the value of the heat of loosening for the self-diffusion of the solvent can be approximately calculated.

3). The heat of loosening  $Q$  is always higher for the self-diffusion of a solvent metal than for the diffusion of any other metal into it, even at low concentrations of the diffusing metal. Thus, as the impurity atoms penetrate into the lattice of the solvent, the heat of loosening becomes lower than that during self-diffusion. The decrease is not gradual with increase in the number of impurity atoms, but is stepwise, even for a small number of impurity atoms.

4). An increase in the concentration of impurity atoms can either increase or decrease the value of  $Q$ .

The increase in the energy required to detach an atom from its equilibrium position with increase in the concentration of impurity atoms is apparently due to the formation of new bonds in the lattice at high concentrations of the diffusing atoms.

\* Blanter /53/ studied the influence of the concentration of carbon in unalloyed austenite on the process of diffusion, and found that the heat of loosening is almost the same in steels containing 0.2, 0.4 and 0.7%, of C:

$$Q = 31,350 \pm 800.$$

However,  $A$  is greatly influenced by the composition of the metal. For example:

$$A = 5.58 \cdot 10^{-2} \text{ cm}^2/\text{sec for } 0.2\% \text{ C};$$

$$A = 7.53 \cdot 10^{-2} \text{ cm}^2/\text{sec for } 0.4\% \text{ C};$$

$$A = 9.63 \cdot 10^{-2} \text{ cm}^2/\text{sec for } 0.7\% \text{ C}.$$

Blanter correlates  $A$  to concentration by the following formula:  $A = 0.04 + 0.08\% \text{ C cm}^2/\text{sec}$ , which shows that an increase in the content of carbon in steel leads to an increase in the diffusion coefficient  $D$ .

## CONCLUSION

1. The first part of this book gives a discussion on the fundamental problems of "atomic" diffusion. In the first chapters we attempted to find the rules governing the diffusion rate of different metals. We also attempted to give a general, although approximate, picture of the processes of diffusion.

The rules found in these chapters are mainly based on the assumption that all diffusion coefficients are equal at the melting point of the same solvent metal.

This assumption is confirmed best by the self-diffusion of a metal, and can be written as follows:

$$\frac{Q}{RT_s} = \text{const.} \quad (\star)$$

The numerical value of the ratio ( $\star$ ) found from experimental data is equal to 20 (or rather between 19 and 20). We based our conclusions on the available data on the self-diffusion of lead, gold, and copper.

The simple relationship between the melting point and the heat of loosening shows that the heat of loosening can be classed with other values which characterize the state of solids, such as: heat of fusion, heat of vaporization, etc. Therefore we were able to apply the known law of corresponding states at the melting point to self-diffusion.

The heat of loosening (or heat of activation) determines the potential barrier which must be overcome by an atom during its passage from one equilibrium position to another, and is becoming more and more used as a characteristic of solids. This characteristic is today introduced in the study of various processes, including those related to changes in the mechanical properties of metals. Therefore, even an approximate assessment of this value for different metals is of considerable practical and theoretical interest.

It has been found that the law of corresponding states can be applied to impurity diffusion in metals. The coefficients of impurity diffusion are usually so close to one another that they can be considered the same, at least within one order of magnitude,

From these considerations a formula was found for the temperature dependence of impurity diffusion.

$$D = \frac{2\delta^2 v_0 Q_0}{RT_s} e^{\frac{Q_1 - Q_0}{RT_s}} e^{-\frac{Q_1}{RT}}. \quad (\star\star)$$

This formula, unlike earlier ones, does not include the heat of loosening  $Q_1$  for impurity diffusion, nor the heat of loosening  $Q_0$  for the self-diffusion of



the solvent, which indicates a quantitative relationship between these two processes.

Although formula (\*\*) is only speculative, it is hoped that this will be a link in the development of a more exact diffusion theory.

The applicability of the law of corresponding states and of formula (\*\*) for impurity diffusion is confirmed because if  $Q_0$  for self-diffusion of the solvent is calculated from data on impurity diffusion using formula (\*\*), the values obtained agree well with one another (for a given solvent) and with experimental results.

Nevertheless, we do not consider that formula (\*\*) is accurate, but believe that basically it is qualitatively accurate. We also believe that this formula can help to open up new research on the diffusion of metals, which we shall discuss later. The equality of the coefficients of impurity diffusion, and consequently the applicability of formula (\*\*), can be used as a criterion for judging the value of the diffusion coefficient and of the mechanism of the process, at least in the range of ordinary temperatures. It can be assumed that the relative value of each of the possible types of the mobility of atoms in the crystal lattice is more or less constant if the law of corresponding states (which determines the "normal" value of the diffusion coefficient) holds, and inversely, a large deviation from this law indicates that the relationship between the different types of mobility is disturbed and one of them is intensified. We know of several cases when the value of  $D_s$  at the melting point is appreciably higher than the "normal" values. For example, in the diffusion of gold and silver in lead, the value of  $D_s$  near the melting point of lead is  $10^{-5} - 10^{-6}$  cm<sup>2</sup>/sec (instead of the usual value for most metals of  $10^{-9} - 10^{-10}$  cm<sup>2</sup>/sec).

Seith earlier maintained that the more rapid diffusion of gold in lead is due to the mobility of gold atoms mainly in the interstices of the lead crystal lattice.

Another example which is very important in practice is the diffusion of carbon in  $\gamma$ -iron.

The recently published paper of Mehl and Wells /54/ indicates that the diffusion coefficient of carbon in  $\gamma$ -Fe near the melting point is about  $10^{-5}$  cm<sup>2</sup>/sec, i. e., the same value as in the diffusion of silver and gold in lead. It is natural to assume that the small carbon atom migrates mainly between the atoms of iron without taking up any regular position in the lattice. This is quite probable, since carbon forms an interstitial solid solution in  $\gamma$ -Fe.

Thus, if we consider as "normal" those values of  $D_s$  which conform with the law of corresponding states, deviations from these values will help us to infer the mechanism of mobility.

The problem of the heat of loosening during impurity diffusion is the most important and complex. We did not attempt to determine this value theoretically, but tried to find the chief factors influencing it. We found that the atomic volumes of the diffusing metals and the coefficient of hydrostatic stress influence this value. The quasiempirical equation relating the heat of loosening during impurity diffusion to the atomic volumes of the diffusing metals and the contraction coefficient of the solvent metal describes many of the experimental results fairly well. The introduction of the idea of a "spatial factor" for diffusion is a development of the earlier theory of Seith on the influence of "relative valencies." These theories are somewhat analogous to the Hume-Rothery rules on the formation of solid solutions.

From the above discussion it can be stated that the chief factors determining the diffusion rate in metals are: the melting point and the contraction coefficient of the solvent metal, and the atomic volumes of both diffusing metals.

2. The rules that we have discussed in this book are only approximate. Their accuracy is limited by the influence of a number of factors which have not been considered during the general study of diffusion processes. The most important of these are related to the structure of the diffusing metals. Therefore, in the following chapters of this book the influence of the structure of metals on the rate of diffusion will be described. These problems have been discussed mainly on the basis of our experimental data.

First, we studied diffusion in metallic single crystals, and determined the dependence of the diffusion rate on the crystallographic direction. Anisotropy of the diffusion rates is observed in crystals of the hexagonal system, but this anisotropy decreases greatly with increase in temperature, and near to the melting point the diffusion rates in different directions are almost equal. This phenomenon, which is understandable if we consider lattice loosening, has not yet been experimentally confirmed. The influence of temperature on the anisotropy of diffusion explains the orientation of phases produced at low temperatures. An example is the formation of lamellar pearlite (with a characteristic orientation of the cementite lamellas) probably the result of a certain supercooling of austenite to temperatures below the eutectoid transformation. It is also believed that the formation of Widmanstätten structures (characterized by the orientation of the precipitate of one of the components of steel) is to a certain extent due to the supercooling of austenite. Another characteristic example of an oriented product of a diffusion transformation is the formation of annealing structures when martensitic steel is annealed at fairly low temperatures. The specific direction of the precipitation of cementite (which coincides with the direction of the initial martensite needles) can be explained by the anisotropy of diffusion.

The next problem we discussed was the "structural sensitivity" of diffusion. Although this problem has not yet been clarified, we can state approximately that at relatively elevated temperatures at which diffusion can be measured the imperfection of the crystal structure is of no great importance. The existence of rules which do not depend on the method of production and treatment of the diffusing metal indicates that diffusion is structurally insensitive.

It can thus be expected that if the law of corresponding states holds for a metal, the structural sensitivity is not important. The self-diffusion of metals conforms to this law best, and should have the lowest structural sensitivity. This has, in fact, been confirmed by direct observations described in a chapter of this book.

The third problem related to structure was the influence of external surfaces which separate individual grains on the diffusion rate.

During a study of this problem we confirmed the well-known fact that with increase in the grain boundaries (i. e., decrease in the grain size) the diffusion coefficient increases. We also found that polycrystalline aggregates have different absolute diffusion coefficients and also different heats of loosening  $Q$  than single crystals. The differences are not so great as to

affect the exponential nature of the temperature dependence of  $D$ , but it is important in itself, since without such a difference it would be difficult to explain the dependence of the absolute value of  $D$  on the grain size.

We explained the influence of the grain size by the greater loosening of the grain boundaries, which leads to a weakening of the intermetallic bonds. There is reason to believe that the influence of the grain boundaries, like that of structural sensitivity in general, is exerted least on self-diffusion.

The influence of the structure on the diffusion rate is noticeable only as we pass from a polycrystalline aggregate to a single crystal. Structural changes in polycrystalline substances which do not entail any phase transformations are small, and can change the diffusion coefficient by not more than one order of magnitude.

3. In the last chapter of Part One we discussed the dependence of the diffusion coefficient on the concentration of the diffusing metal. The conclusions will not be repeated here, as they were formulated quite clearly.

4. The purpose of the first part of this book was to study diffusion in metals experimentally and clarify its main aspects. We do not yet have any experimental basis for determining the mechanism of the mobility of atoms in crystal lattices. We can only make assumptions as to which type of mobility (of the three mentioned above) is predominant in a particular case. Thus, we believe that a number of experimental data indicate that the predominant type of mobility during self-diffusion of pure metals is direct interchange of pairs of atoms. This opinion is supported by the simple relationship between the heat of loosening and the melting point, which is identical for all metals so far studied, by the low coefficient of self-diffusion and correspondingly high value of  $Q$ , by the lack of a tangible structural sensitivity of this phenomenon, and by the small influence (as far as this could be determined) of the external surfaces. From the above we can conclude that the mobility of atoms in their own lattice is very regular and slow. Thus, these conditions are best described by direct interchange of pairs of atoms.

On the other hand, we found that the diffusion of an impurity metal has a very high diffusion coefficient, which does not agree with the existing rules (for example, diffusion of carbon in iron). It is possible that in such cases other types of mobility predominate, which accelerate the process. Such types include interstitial and vacancy mechanisms. In all other ("normal") cases of impurity diffusion there is, apparently, a certain relationship between all processes of atom exchange. The discovery of these will make it possible to develop a more complete theory of diffusion.



*Chapter I*

*NATURE OF PHASES FORMED AS A RESULT  
OF REACTIVE DIFFUSION*

**§ 1. Determination of possible diffusion beyond  
the solubility limits**

The specific feature of atomic diffusion that we discussed in the first part of this book is that it results only in a change in the concentration of the solid solution formed in the lattice. This change determines the structure and the properties of the product formed on the surface of the basis metal as a result of diffusion.

However, it is possible that microstructural studies of such a surface will not reveal any noticeable changes in the starting basis metal, since the structure of the solid solution formed does not differ from that of the solvent metal. In such cases the diffusion layer is not separated from the basis metal by any sharp boundary, and only careful etching may approximately show the depth of penetration of the diffusing atoms.

However, sometimes atomic diffusion appreciably changes the structure of the surface layer. This happens if an increase in the concentration of the solid solution at elevated temperatures involves a phase transformation during the cooling of the diffusion layer and precipitation of new structural components. An example of such a process is cementation of iron, in which the solid solution (austenite) formed decomposes as a result of cooling into a mechanical mixture of ferrite and cementite. Thus, in this process a new phase, cementite or iron carbide  $\text{Fe}_3\text{C}$ , is formed. However, we classify this process as atomic diffusion, since the new phase is not formed as a result of diffusion, but through additional processes associated with phase transformations as a result of cooling.

Therefore, the process of atomic diffusion should be defined as one which does not involve the formation of new phases as a result of direct diffusion. It is certain that atomic diffusion can take place up to a certain concentration only (solubility limit) of the diffusing metal in the lattice of the solvent metal. Some authors, for example, Guillit and Bernard /57/, believe that this is a necessary condition for any diffusion, which means that they considered atomic diffusion as the only possible type in solid metals.

Today, the erroneousness of this assumption is obvious. The appreciable amount of accumulated experimental data, and numerous industrial processes on the surface treatment of metals, indicate that inter-

\* The first and second chapters on the reactive diffusion of metals were written together with D. Gluskin.

diffusion of metals is possible to concentrations many times that of the limiting solid solutions formed by each of the diffusing metals. Obviously, this can occur only as a result of the formation of new phases at the contact boundary of the metals. The crystal lattices of these phases are different from those of the starting metals. This type of diffusion we shall call reactive diffusion.

We should like to point out that these terms are relative, since chemical interaction between atoms can take place in ordinary solid solutions also, and this determines the dependence of the diffusion coefficient on the concentration. However, we shall employ these terms because of their wide usage.

Most industrial processes related to the heat treatment of metals are based on reactive diffusion. We should include, for example, carburizing and nitriding of iron, hot-dip tin and zinc coating, etc. These processes show the actuality of the problems of diffusion.

Possible diffusion beyond the solubility limits was mentioned by Charpy in 1903 /58/. He found that cementation of iron in potassium cyanide at 650°C can increase the concentration of carbon on the surface of iron to 6.72%. Since at this temperature only  $\alpha$ -iron exists, which dissolves almost no carbon, the results of Charpy could be explained by either the saturation of the surface of iron with free carbon, or the formation of a new carbon-rich phase, such as iron carbide ( $\text{Fe}_3\text{C}$ , containing 6.67% of carbon).

The results of Charpy were confirmed and verified by Zing /59/, who experimented on the cementation of iron and steel specimens at 670–690° and 780–800°C. A study of the microstructure of the specimens showed that in steel specimens a continuous layer of cementite is formed, with a sharp boundary dividing it from the bulk of the metal.

In one of the experiments at 670–690°C, a very thin steel sheet (0.05 mm) was completely transformed into cementite.

The term "reactive diffusion" was introduced by Fry /60/, who studied the diffusion of phosphorus, silicon, nickel, manganese, and sulfur in iron. He gave his results in the form of curves in concentration – depth of penetration coordinates. He found that phosphorus and silicon give curves which are rather different from those for the diffusion of sulfur, manganese, and nickel in iron, and hence concluded that the diffusion of nickel, sulfur, and manganese in iron is different from that of phosphorus and silicon. He believes that the diffusing element exists in the lattice of the solvent metal as molecules of a compound with iron, and not as atoms. Thus, the diffusion of phosphorus in iron yields a chemical compound  $\text{Fe}_3\text{P}$ , which enters the iron lattice as whole molecules. This explains the specific shape of the curve obtained. The process of diffusion can thus lead to the formation of molecular solid solutions. Fry called this process reactive diffusion, in contrast to atomic diffusion.

The mechanism suggested by Fry to explain the shape of the diffusion curve cannot be considered satisfactory for a number of reasons, mainly because of the hypothesis on the existence of molecular

solid solutions in metallic systems.\* Prokoshkin /62/ analyzed Fry's results. He showed that the shape of the concentration curve for silicon and phosphorus is due to phase transformation and not to the molecular nature of the solid solutions formed.

The formation of intermetallic phases as a result of diffusion in solids has been confirmed by many authors including Prof. Tsigler and co-workers /63/, Laissus /64/, Grube /65/, Jones /66/, Eisenhutt and Kaypp /67/, and others, who studied the diffusion of iron, and by Elam /29/, Weiss /68/, Oknov /69/, Bugakov and Gluskin /70/, and many others, who studied diffusion in different metals. The only condition for the formation of new phases as a result of diffusion is that the substances participating in this process must be able to form intermetallic compounds. The existence of this ability can be determined from the phase diagram of the diffusing metal.

Even if the phase diagram indicates that both solutions and also different intermetallic compounds can exist in a given system, there remains the problem of the sequence of formation of these phases during diffusion.

It is widely believed that during the diffusion of two metals an intermetallic phase can be produced only after the basis solid solution has been saturated with the diffusing metal. This is emphasized in the paper of Prokoshkin on the diffusion of different elements in iron. This author points out that reactive diffusion is accompanied by the formation of a solid intermetallic compound, and starts after the saturation limit is reached in the end solvent layer. This point of view has no theoretical foundation and is contradicted by a large number of experimental data, including our own results, which we shall discuss later. According to Prokoshkin and other authors who share his ideas, the formation of a new phase (intermetallic compound) as a result of diffusion involves only a rearrangement of the lattice when the solubility limit is reached in the basis solid solution. This approach denies the existence of reactive diffusion, since the process is based solely on phase transformations.

It seems to us that the principle underlying reactive diffusion is that contact between two metals may lead to a chemical reaction, irrespective of mutual solubility, and the formation of an intermetallic compound directly at the interface.

However, it is impossible to predict the nature of the intermetallic compounds formed,\*\* since their structure and composition are clearly determined by a number of factors, including the structure of the reacting metals, the state of their surface, the temperature of reaction, the pressure, presence of impurities, etc.

\* The problem of the existence of molecular solid solutions is beyond the scope of this book, and we shall not discuss it here in detail. We should only like to point out that recently research workers believe that even if the lattice of the solvent metal contains a combination of atoms resembling molecules, the lattice is not penetrated by the whole molecules, but only by atoms. In this connection the work of Mehl and Rhines /61/ on the diffusion of silicon and nickel in copper is interesting. The authors found molecules in the lattice of copper, but explained this by the formation of "short-lived" bonds between the atoms of Ni and Si in neighboring positions in the lattice of copper, and not by the penetration of whole molecules into the lattice.

We should also like to mention the paper of Moroz /71/, who studied the diffusion of a number of carbides in iron, and found that atoms produced as the result of dissociation of compounds, and not whole compounds, diffuse into the lattice of the metal.

\*\* It is also clear that such compounds should correspond to the phase diagram of alloys of the reacting metals.

If we first assume that a reaction between atoms of two metals starts with adsorption, then in analogy with the processes taking place at the metal-gas interface we can relate reactive diffusion to activated adsorption or chemisorption, in which chemical forces of interaction are active. Such adsorption, which is not really a chemical process, is the initial stage of surface reactions. The possibility of such a reaction was indicated by Langmuir and others. As an analogy we can say that chemisorption is a necessary preliminary stage in the formation of a new intermetallic phase on the boundary between two metals as the result of diffusion. The heat of activation of adsorption is of the same order of magnitude as the heat of "loosening" during diffusion, but the heat of physical adsorption is appreciably lower.

Until now we have discussed the formation of new phases as the result of diffusion in solid metals. However, the formation of new phases between a solid and a liquid metal is also of great theoretical and practical importance. Such reactions take place, for example, during hot-dip zinc and tin coating, calorizing of iron, lead-coating of iron, tin-coating of copper, etc. Although these operations seem to be simple, and include only the immersion and holding of the solid high-melting metal (iron, copper) in the low melting melt (tin, zinc, lead, aluminum), the production of good, well-adhering deposits is quite difficult.

Due to their complexity, the numerous processes taking place during the interaction between solid and liquid metals are rather difficult to investigate, and therefore reactive diffusion in them has been little studied.

The processes occurring during the dissolution of a high-melting solid metal in a low-melting liquid metal are more complex than diffusion between two solid metals, since such a dissolution involves a direct chemical reaction on the interface of the two metals, with the formation of intermediate layers of alloys corresponding to the phase diagram of a given system. In such processes the formation of intermetallic phases may be the result of a dissolution process only.

Let us consider the simplest case, when the high-melting metal dissolves in the low-melting one and there is no reaction at the interface. Such cases can be described as follows:

If a high-melting metal *A* is immersed in a low-melting metal *B*, the particles of *A* pass into the liquid solution. The concentration of *A* in the liquid will increase with time, at a rate determined by the rate of diffusion of *A* in *B*.

If the temperature of the liquid metal is not much higher than the melting point of *B*, and the holding time is not too long, then in still baths there will be a rather large change in the concentration of the liquid metal in a relatively thin layer near the solid metal, and the concentration in this will reach saturation in a certain period of time. This will lead to crystallization of a new phase from the melt. The composition and structure of this phase will correspond to the equilibrium conditions at a given temperature, and consequently to the phase diagram of metals *A* and *B*. If metals *A* and *B* do not form intermetallic phases, and their phase diagram is similar to that shown in Figure 21, the saturation of the liquid alloy by metal *B* will correspond to point *C* on the diagram (at a concentration equal to  $k\%$  of *A*).



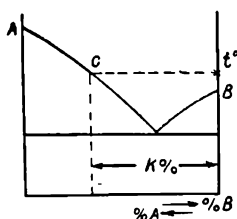


FIGURE 21. Phase diagram of a system with no intermetallic compounds.

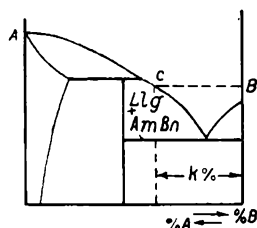


FIGURE 22. Phase diagram of a system with intermetallic compounds.

If a constant temperature  $t^\circ$  is maintained, the dissolution will stop, and crystals of metal  $A$  will be precipitated from the liquid alloy. Some of these will remain in the melt and some will crystallize on the surface of the solid metal.

After a sample of metal  $A$  is removed from the melt, the adhering liquid layer will solidify to form an alloy with a structure corresponding to point  $C$  on the phase diagram, and consisting of an  $(A+B)$  eutectic plus an excess of crystals of metal  $A$ . Such a structure was obtained by Oknov /69/.

If the two reacting metals are able to form intermetallic compounds, i. e., if their phase diagram is similar to that shown in Figure 22, \* then the dissolution of the high-melting metal  $A$  in the liquid metal  $B$  will produce crystals of the intermetallic compound  $A_m B_n$  when the maximum concentration of the liquid is reached (at temperature  $t^\circ$ ). Some of these crystals will also be present in the liquid alloy and will crystallize on the surface of the solid metal  $A$ . In this case the structure of the surface layer should correspond to that of an alloy represented by  $C(k\% \text{ of } A)$ , and will consist of crystals of the intermetallic phase  $A_m B_n$  and a eutectic  $(A_m B_n + B)$ . The crystals of  $A_m B_n$  which nucleate on the surface of the high-melting metal will probably grow perpendicular to that surface in the direction of the low-melting metal.

Similar structures have been obtained during a study of the reaction of iron with liquid zinc, which we shall discuss later.

The above case of the formation of an intermetallic phase during the dissolution of a high-melting metal in a low-melting one is of course not the only one. However, the low-melting metal does not always form a eutectic, but often a saturated solid solution or other phases, and the structure of the surface layers varies accordingly. This structure should describe the condition of equilibrium at the boundary between the liquid and solid metals, that is corresponding to the phase diagram of alloys of a given system.

We very often have systems of two metals which form several intermetallic phases. The interaction between such metals will produce several intermediate layers.

If we assume that equilibrium conditions exist, and that the process of dissolution is the one which determines the structure of the diffusion layer, we conclude that the first phase formed in this process is the one that can

\* In the simplest case when only one intermetallic compound is formed.

exist at a given temperature in equilibrium with a liquid solution. Such a phase should have the lowest melting point of all the phases that can be formed in a given system and under given conditions.

The formation of other phases of this system should be considered to be the result of interaction between the initially formed low-melting phase and the basis (solid) metal.

Thus, we can consider the interaction between a solid and a liquid metal on the basis of dissolution only. This interaction can lead to the formation of intermetallic phases, but as a result of the saturation of the liquid layer adjacent to the solid by the high-melting metal. This indicates that these phases are diffusional in nature and not reactive. Such a process is very similar to the formation of new phases by the decomposition of solid solutions formed when one solid metal diffuses into another (for example, cementation of iron), which we discussed at the beginning of this chapter.

We should now determine whether the above mechanism of formation of intermetallic phases during the reaction between liquid and solid metals is the only possible, or whether there are other similar processes, such as direct chemical reaction at the interfaces of two metals.

These questions can be answered by studying the nature of the phases produced at the interfaces of liquid and solid metals and the sequence of their formation. If this study shows that at the beginning of the reaction a phase can be formed which is not in a state of equilibrium with the liquid at a given temperature (that is a phase which does not have the lowest melting point of all intermetallic phases of a given system), this would prove the existence of a purely reactive process, not directly connected with the process of dissolution. The process of dissolution in such a case would change, since the formation of an intermetallic layer would greatly hinder the access of liquid metal to the high-melting solid from the start of the process, and this would appreciably decrease the rate of dissolution. Thus, another possible method for determining the nature of the interaction between liquid and solid metals is a study of the kinetics of the processes.

The above theory on the nature of the diffusion layer produced by processes occurring during such diffusion is true also when both metals are in the solid state. Therefore, we believe that the question of the nature of the phases produced by reactive diffusion, and the sequence of their formation, is fundamental.

## **§ 2. The nature of the phases formed as the result of reactive diffusion**

There are many data on the intermediate intermetallic phases produced by an interdiffusion of metals. The interactions between two solid metals has been studied best. This problem is also considered in most of the papers mentioned above.

There are fewer published data on the problem of the interaction between solid high-melting metals and liquid low-melting metals. The principal ones in this field are those of Tamman and Rocha /72/ and Oknov. There are also a number of studies on the more specific problems of the hot-dip coating of metals (for example, zinc coating), which we shall discuss later.

In these studies microstructural analysis was the chief method for studying the physicochemical nature of the phases produced by diffusion. In many cases this method alone is insufficient, and therefore there were contradictions between the results of different authors. For example, Tamman and Rocha studied the interdiffusion of copper and zinc, and found  $\epsilon$ -,  $\gamma$ -, and  $\beta$ - phases, while Mazing, who studied the diffusion of these metals, found no  $\epsilon$ - and  $\gamma$ - phases. There is no certainty about other metals either. Therefore, the purpose of this research was to determine as accurately as possible the nature of the diffusion phases by different methods.

One of the few existing systematic studies on diffusion in a large number of binary systems is that of Oknov /69/.

This author believes that the immersion of a high-melting metal into a liquid low-melting metal is followed by the formation of a phase which is rich in the low-melting substance, and therefore exists in a state of equilibrium with the liquid.

## I. Interdiffusion in Cu - Zn and Fe - Zn systems

a. Materials studied and experimental methods. To study the nature of the phases formed as a result of the interdiffusion of metals we chose the Cu-Zn and Fe-Zn systems, since both produce characteristic intermetallic phases with structures governed by the Hume-Rothery laws, or in other words, with a certain electron concentration.

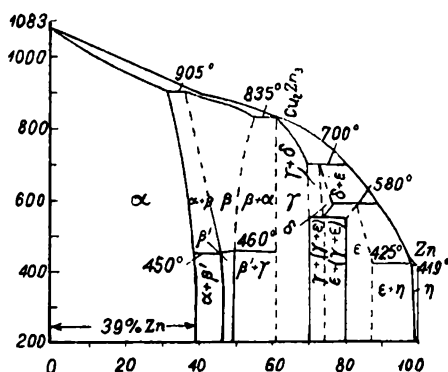


FIGURE 23. Cu-Zn phase diagram.

Figure 23 shows the phase diagram of Cu-Zn alloys according to Bauer and Hansen. It can be seen that the system contains the following phases:  
 $\alpha$  - a solid solution of zinc in copper with a copper lattice;  
 $\eta$  - a solid solution of copper in zinc with a zinc lattice;

$\beta$  — a phase with a composition close to that of the Cu—Zn intermetallic compound with a centered cubic lattice, which exists in the range from 40 to 47 wt% Zn;

$\gamma$  — a phase with a composition corresponding to the  $\text{Cu}_5\text{Zn}_8$  compound\* with a face-centered cubic lattice containing 52 atoms in the unit cell. It exists in the range from 59 to 67 wt % Zn.

$\epsilon$  — a phase with a composition close to that of the  $\text{CuZn}_3$  compound with a close-packed hexagonal lattice, which exists in the range from 78 to 86 wt% Zn.

The  $\beta$ -,  $\gamma$ - and  $\epsilon$ -compounds are typical Hume-Rothery phases, and have the same electron-to-atom ratio. This ratio is  $3/2$  for the  $\beta$ -phase,  $21/13$  for the  $\gamma$ -phase, and  $7/4$  for the  $\epsilon$ -phase.

These phases can exist at any temperature below the melting point, but the phase diagram predicts a  $\delta$ -phase in the Cu—Zn system which exists at temperatures from 555 to 700°C. Below 555°C the  $\delta$ -phase decomposes into a eutectoid mixture ( $\gamma + \epsilon$ ).

The Fe—Zn system contains two intermetallic compounds, corresponding approximately to  $\text{Fe}_5\text{Zn}_{21}$  and  $\text{FeZn}_7$ . The first has a ratio of valence electrons to atoms of  $21/13$ , and the second a ratio of  $7/4$ .

The interdiffusion of copper and zinc and of iron and zinc has been studied in solid and liquid zinc.

The starting materials were electrolytic copper 99.9% pure, commercially pure zinc distilled several times in vacuo, and electrolytic iron containing 0.04% of carbon

To study the layers formed during the interdiffusion of copper and liquid zinc, the copper specimens (4 mm in diameter and 25 mm high) were immersed in molten zinc and held for different periods of time and at different temperatures. To prevent oxidation of the liquid bath, a mixture of  $\text{BaCl}_2$  and  $\text{CaCl}_2$  was periodically added. To test this addition, we carried out several control experiments in vacuo, and the results were the same as those obtained in the ordinary way.

To study diffusion between two solid metals, the zinc specimens (4 mm in diameter) were electrolytically coated with copper, sealed into evacuated glass ampules, and held at different temperatures for different periods of time.

The same general method was used to study the interdiffusion of iron and zinc but for diffusion in solids the iron specimens were coated with zinc and heated to different temperatures below the melting point of zinc. Microstructural analysis showed that the coating of the iron specimens did not lead to any appreciable diffusion (absence of diffusion layer).

In all experiments the temperature was measured by an Ni—NiCr thermocouple, and during prolonged experiments the temperature was maintained constant within 0.1°C by a temperature regulator of the Kovalski-Strelkov system.

The structure and composition of the diffusion layers were determined by microstructural, X-ray, and chemical analyses, and also by measuring the hardness of the specimens (the chemical analysis and the hardness measurements were carried out in studies on the diffusion of copper in zinc).

\* Sometimes this compound is given as  $\text{Cu}_2\text{Zn}_3$ , but from the structural point of view,  $\text{Cu}_5\text{Zn}_8$  is more correct.

b. **Microstructural study of the nature of Cu—Zn diffusion layers.** As etchants for these studies we used a 1% aqueous solution of ammonium persulfate and a 6% solution of ferric chloride in 10% HCl.

Very short-time heating of copper in liquid zinc and relatively short-time heating of solid copper in contact with solid zinc gave only one bright layer at the interface.

If the temperature is increased this layer grows, and another gray one appears near the zinc. After prolonged heating at elevated temperatures a third yellow layer appears near the copper. Plate 2 in the Appendix shows all three diffusion layers produced by heating copper and zinc for 7 hours at 430°C.

It is clear that a microstructural analysis alone cannot completely answer the questions on the phase and chemical compositions of diffusion layers, but some assumptions can be made. Not one of the three layers contains  $\alpha$ - and  $\eta$ -phases, since these layers are formed by atomic diffusion of zinc in the lattice of copper and of copper in the lattice of zinc. This assumption was confirmed by Banister and Jones /73/ and by Jones /66/, who found that the diffusion of two metals produces a layer separated from these metals by a boundary only when the physicochemical nature of this layer is very different from that of the starting metals.

If we exclude  $\alpha$ - and  $\eta$ -phases, we can assume from the phase diagram that the three layers formed by diffusion are  $\beta$ -,  $\gamma$ - and  $\epsilon$ -phases. It is certain that the yellow layer next to the copper consists of a  $\beta$ -phase. It can be assumed that the bright middle layer consists of a  $\gamma$ -phase, and the gray layer near the zinc (or, more accurately, near the  $\eta$ -solid solution of copper in the lattice of zinc), but separated from it by a well-marked boundary, consists of an  $\epsilon$ -phase. This preliminary determination of the phase composition of diffusion layers shows that the bright layers produced at the beginning of diffusion before the other layers are formed consist of a  $\gamma$ -phase.

To study the interdiffusion of iron and zinc we used a 4% solution of nitric acid in alcohol as an etchant.

The microstructure showed that under all experimental conditions the following two layers are formed: 1) a light layer (sometimes acicular) near the iron, and 2) a light yellow layer with elongated digital grains near the zinc (see Appendix, Plate 3). The Fe—Zn phase diagram indicates that the layer adjacent to the iron is a  $\gamma$ -phase ( $\text{Fe}_5\text{Zn}_{21}$  intermetallic compound) and the layer adjacent to the zinc is an  $\epsilon$ -phase ( $\text{FeZn}_7$  intermetallic compound).

c. **Study of the hardness of diffusion layers.** The measurement of hardness for determining the nature of diffusion layers has been used for studying the interdiffusion of copper and zinc only. For the Fe—Zn system this method has not been used, since the preparation of master iron—zinc alloys with an exact composition is difficult because of the intense evaporation of zinc at elevated temperatures. Also, the determination of the nature of the diffusion phases is not difficult in these systems.

To find the phase composition by measuring the hardness of diffusion layers in Cu—Zn systems, a series of master alloys was prepared corresponding to certain phases of this system. A chemical analysis of the alloys gave the following zinc content: 65.7% ( $\gamma$ -phase), 83% ( $\epsilon$ -phase),

and 99.2% ( $\eta$ -phase). For hardness measurements we took three specimens of each of the above alloys. The Martens hardness test was used, in which the surface is scratched by a conical steel point loaded with 100 g, and the width of the scratch is measured by a microscope. The results are given in Table 37.

TABLE 37. Hardness of different phases of the Cu-Zn system

No. of sample	Zn %	Phase	Width of scratch, $\mu$	Mean width of scratch, $\mu$
1	65.7	$\gamma$	30	30
2			31	
3			28	
4	83.0	$\epsilon$	54	50
5			47	
6			50	
7	99.2	$\eta$	63	69
8			74	
9			70	

The hardness of the master alloys and of the diffusion layers is measured by the same method and under the same conditions. The results are given in Table 38.

TABLE 38. Hardness of diffusion layers

No. of sample	Width of scratch, $\mu$			No. of sample	Width of scratch, $\mu$			No. of sample	Width of scratch, $\mu$		
	yellow layer	light layer	gray layer		yellow layer	light layer	gray layer		yellow layer	light layer	gray layer
1	—	30	—	8	54	32	48	13	—	28	—
2	—	30	53	9	50	29	—	14	—	29	45
3	—	29	52	10	50	30	47	15	51	27	46
4	—	27	55	11	54	30	49	16	50	29	48
5	—	32	55	12	53	29	50	17	50	28	—
6	—	28	54	—	—	—	—	—	—	—	—
7	—	27	53	—	—	—	—	—	—	—	—
Diffusion in the liquid state								Diffusion in the solid state			

A comparison between Tables 37 and 38 shows that the width of the scratch on the light diffusion layer is closest to that on the master alloy containing 65.7% Zn ( $\gamma$ -phase). The width of the scratch on the gray layer next to the zinc ( $\eta$ -solid solution) is the same as that on the alloy with 83% Zn ( $\epsilon$ -phase).

Thus, hardness measurements confirm that the compositions of the diffusion layers are the same as those assumed from the results of microstructural analysis.

d. **Chemical analysis of diffusion layers.** To determine the chemical composition of the phases formed as a result of the interdiffusion of copper and zinc, a copper specimen was held in liquid zinc at 600°C for a long time. As a result (see microstructure, plate 2) all three layers were formed. The bright one in the middle was the most extended.

The specimen was taken from the bath and a 0.1–0.2 mm layer removed by a lathe. The turnings were analyzed. Table 39 and Figure 24 show the percent of zinc as a function of the mean thickness of the sample.\*

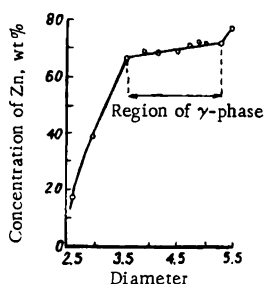


FIGURE 24. Variation in the composition of copper-zinc diffusion layers.

TABLE 39. Chemical composition of diffusion layers formed by the interaction of Cu and Zn at 600°C

No. of turnings	Mean thickness of specimen	Content of Zn, %	Phase
3	5.5	76.6	δ
4	5.29	71.9	
6	5.04	71.8	
7	4.9	71.3	γ
8	4.78	71.3	
9	4.54	69.3	
10	4.19	68.2	
11	3.89	68.3	
12	3.62	68.3	β
14	2.95	38.4	
15	2.63	17.5	α
16	2.4	0	Cu

The above data indicate that the composition of the diffusion layers corresponds to that of the γ-phase to an appreciable depth, and therefore the thickest bright middle layer found by microstructural analysis is also part of this phase.

e. **Identification of phases by X-ray analysis.** Westgren /74/ widely studied the Cu–Zn system by X-ray analysis, and found that the β-phase

- By the mean thickness we understand the mean arithmetic thickness of the sample before and after removal of the upper layer.

has a centered cubic lattice with a parameter  $2.95\text{ \AA}$ , the  $\gamma$ -phase has a complex cubic lattice with 52 atoms in the unit cell, and a parameter varying from  $8.85$  to  $8.89\text{ \AA}$ , depending on the composition, and the  $\epsilon$ -phase has a close-packed hexagonal lattice with  $\frac{c}{a} = 1.55$ .

The Japanese chemists Osawa and Ogawa /75/ carried out similar studies on the Fe—Zn system, and found two chemical compounds:  $\text{Fe}_3\text{Zn}_{10}$  (accurately,  $\text{Fe}_5\text{Zn}_{21}$ ), and  $\text{FeZn}_7$ . The  $\text{Fe}_3\text{Zn}_{10}$  compound ( $\gamma$ -phase) has the same lattice as the  $\gamma$ -phase of the Cu—Zn system, and its parameter varies from  $8.89$  to  $8.93\text{ \AA}$ . The  $\text{FeZn}_7$  compound ( $\epsilon$ -phase) has a close-packed hexagonal lattice with  $\frac{c}{a} = 1.607$ .

To study the X-ray structure of diffusion layers, turnings were removed from the specimens by a lathe, and pressed into  $1\text{ mm}$  high bars, that were then analyzed by the Debye method.

The target was made of iron with a wavelength of  $\lambda k_\alpha = 1.932\text{ \AA}$  and  $\lambda k_\beta = 1.753\text{ \AA}$ .

The X-ray camera for analyzing Fe—Zn alloys had a diameter of  $57.3\text{ mm}$ , and the camera for Cu—Zn specimens a diameter of  $55.4\text{ mm}$ . The lines of the X-ray photographs were indexed by comparing the reflection angles calculated from these lines with those obtained by Westgren, and Osawa and Ogawa in the papers we discussed above. The indexing was also partially based on the atomic factor.

The Bragg formula was used in the calculations

$$a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \frac{\theta}{2}} \text{ for cubic lattices}$$

and

$$a = \frac{\lambda \sqrt{\frac{3}{4}(h^2 + k^2 + hk) + \frac{l^2}{c^2}}}{2 \sin \frac{\theta}{2}} \text{ for hexagonal lattices.}$$

To calculate the lattice parameter, the Kurdymov correction for absorption was introduced.

The deciphering of the X-ray photographs showed that diffusion in Cu—Zn systems at elevated temperatures and for prolonged periods yields  $\beta$ -,  $\lambda$ -, and  $\epsilon$ -phases. The layers close to zinc (the first turnings) contain mainly the  $\epsilon$ -phase. Closer to the copper the intensity of the  $\epsilon$ -lines decreases, and lines of the  $\gamma$ - and  $\beta$ -phases appear.

An X-ray analysis of the diffusion layers formed in the Fe—Zn system indicated the presence of  $\gamma$ - and  $\epsilon$ -phases ( $\text{Fe}_5\text{Zn}_{21}$  and  $\text{FeZn}_7$  intermetallic compounds).

f. Discussion of the results obtained during diffusion in Cu—Zn and Fe—Zn systems. A comparison of the results of microstructural, chemical and X-ray analyses of diffusion layers, and the results of hardness measurements, indicated the following:

1. Prolonged diffusion in the Cu—Zn system leads to the formation of distinctly separated layers. The layer closest to zinc turns gray when



etched in a 1% solution of ammonium persulphate, and contains an  $\epsilon$ -phase. The light, bright layer next to it consists of a  $\gamma$ -phase, and the yellow layer next to the copper, a  $\beta$ -phase.

The first phase formed by diffusion in the solid state is the  $\gamma$ -phase, which is also the only one at low temperatures of diffusion. It is also possible that the  $\gamma$ -phase is the first formed during diffusion in liquid zinc.

Finally, it is certain that the  $\beta$ -phase is formed after the  $\gamma$ - and  $\epsilon$ -phases.

2. Diffusion in Fe—Zn leads to the formation of distinctly separated layers. The layer closest to zinc is an  $\text{FeZn}_7$  compound ( $\epsilon$ -phase), and the layer closest to iron is an  $\text{Fe}_5\text{Zn}_{21}$  compound ( $\gamma$ -phase).

The most important results were obtained by studying the interdiffusion of copper and zinc in the solid state and when the low-melting metal was liquid.

As we have already mentioned, the first phase formed by diffusion in liquids (at  $150-450^\circ$ ) is always the  $\gamma$ -phase, which does not border directly on copper, on zinc, or on their solid solutions.

Thus, it is possible that the interaction between two solid metals leads to the formation of intermetallic phases which do not conform to the maximum solubility in the lattice of the diffusing metals. This contradicts the theory of Prokoshkin and others, who consider that new phases are formed during diffusion only as the result of saturation of the basis (limiting) solid solutions.

These intermediate phases may be formed by a direct chemical reaction on the interface of the diffusing metals. The formation of such phases is a characteristic example of reactive diffusion.

A  $\gamma$ -phase is also formed during the reaction between copper and liquid zinc. This is indicated by the formation of a  $\gamma$ -layer only on the interface during the first moments of the reaction, but an  $\epsilon$ -phase alone has never been found. Here too, an intermediate phase is first formed, which is not the phase in a given system with the lowest melting point, or in other words it is not in a state of equilibrium with the liquid alloys. This indicates that a reactive process can take place during the reaction between a high-melting metal and a liquid low-melting metal.

The order of formation of phases during the interdiffusion of iron and zinc could not be determined. Both phases appear together in the structure of the diffusion layer. Therefore, we shall discuss the interaction between these two metals in a separate chapter.

Since we found that the conditions of equilibrium have no great influence on the nature of the reactive phases formed at the beginning of diffusion, we should expect that a certain influence is exerted by the energy conditions, such as the heat of formation. To check this assumption it was necessary to obtain new experimental data on other metal systems. We chose the Ag—Zn, Ag—Cd, and Cu—Cd systems, since they contain intermetallic phases of similar structures (Hume-Rothery phases), and this facilitates comparison between the results of the study and generalization.

## II. Interdiffusion in Ag—Zn, Ag—Cd and Cu—Cd systems

a. Materials studied and experimental methods. An X-ray analysis\* showed that in Ag—Zn, Ag—Cd, and Cu—Cd systems the following

\* A summary of the results of X-ray analyses of these systems carried out by different authors is given in the 1931 issue of the *Strukturberichte*.

compounds\* can be formed:

#### Ag—Zn

- $\alpha$  — solid solution of zinc in silver containing 0—38 at. % Zn;
- $\beta$  — solution (above 264°C) which corresponds to an AgZn compound with a face-centered cubic lattice ( $a = 3.16 \text{ \AA}$ ) containing 50—54 at. % Zn;
- $\gamma$  — solution corresponding to an Ag<sub>5</sub>Zn<sub>8</sub> compound with a cubic lattice containing 52 atoms per unit cell ( $a = 9.327 \text{ \AA}$ ); this solution contains 59—63 at. % Zn;
- $\epsilon$  — solution corresponding to an AgZn<sub>3</sub> compound containing 69—85 at. % Zn; it has an hexagonal close-packed lattice ( $a = 2.82 \text{ \AA}$ ,  $c = 4.46 \text{ \AA}$ );
- $\eta$  — solid solution of zinc in silver with a zinc lattice.

#### Ag—Cd

- $\alpha$  — solid solution of cadmium in silver with a silver lattice; contains 0—44 at. % Cd;
- $\beta$  — solution (above 426°C) corresponding to the AgCd compound; contains 49—51 at. % Cd;
- $\gamma$  — solution close to the Ag<sub>2</sub>Cd<sub>3</sub> compound. It has a lattice analogous to that of the  $\gamma$ -phase of the Ag—Zn and Cu—Zn alloys; contains 54—65 at. % Cd;
- $\epsilon$  — solution corresponding to the AgCd<sub>3</sub> compound, with a close-packed hexagonal lattice; contains 67—83 at. % Cd (according to other sources 67—90 at. % Cd);
- $\eta$  — solution of silver in a cadmium lattice.

#### Cu—Cd

The Cu—Cd system has not yet been fully studied. The cadmium-rich side has two phases:

- $\gamma$  — phase corresponding to the Cu<sub>5</sub>Cd<sub>8</sub> compound; contains 70—77 wt. % Cd;
  - $\epsilon$  — phase corresponding to the CuCd<sub>3</sub> compound; contains 84—86 wt. % Cd.
- As starting materials we used electrolytic Cu (99.9% pure), "Kalbaum" Cd, vacuum distilled commercially pure Zn, and 99.5% pure Ag. The diffusion of Ag in Zn and in Cd, and of Cu in Cd was studied for both solid and liquid low-melting components.

The carefully cleaned and etched high-melting specimens (Ag—Cu) were immersed in the molten metal (Zn, Cd) and held for a certain time at a given temperature. To avoid oxidation, the melt was covered by a mixture of BaCl<sub>2</sub> and CaCl<sub>2</sub>, and sometimes by ground charcoal powder.

To study diffusion in solid metals, the zinc and cadmium specimens were electrolytically coated by silver and copper, and heated for different periods of time at a given temperature.

\* The designations of the individual phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\epsilon$ , and  $\eta$ ) we adopted is normally used in X-ray studies (according to Hume-Rothery, Westgren, and others). These designations are often different from those given in the corresponding phase diagrams. The data of X-ray analysis may also differ from the known phase diagram obtained by other methods. This is true for the Ag—Zn and Ag—Cd systems, as the phase diagrams indicate the existence of  $\delta$ -phases which have not been found by X-ray studies.

The nature of the layers formed during diffusion and the kinetics of their growth were studied by microstructural and X-ray analyses, which we have already discussed.

b. Studies of the microstructure of diffusion layers. After the specimens had been heated, samples were prepared for microstructural studies. The surfaces of the samples were etched in a 4% solution of nitric acid in ethyl alcohol.

The diffusion layers were usually visible without etching and etching only revealed the phase boundaries more clearly.

Diffusion in the Cu—Cd system below 400°C at first produced only one layer between the copper and cadmium, which continued to grow with time. When the heating was prolonged, another narrow, bright layer appeared, with sharply defined boundaries. By heating above 400°C, only one layer of this same structure was produced, irrespective of the duration of heating (see Plate 4 in the Appendix).

The location, etchability and nature of the diffusion layers indicate that the first layer bordering on cadmium is an  $\epsilon$ -phase ( $\text{CuCd}_3$ ), and the second layer formed later, which borders on copper, is a  $\gamma$ -phase ( $\text{Cu}_5\text{Cd}_8$ ).

When Ag—Zn systems were heated at 450°C for 40 sec, three layers were formed which could be seen under a microscope.

Since X-ray analysis showed that the Ag—Zn system can contain only three intermetallic phases, the order of their location indicates the nature of each. The layer closest to zinc is an  $\epsilon$ -phase, and those farther away are a  $\gamma$ - and  $\beta$ -phase, respectively. The middle layer is the narrowest one.

When diffusion in solids occurred at 400°C after two hours three layers were formed, which were, however, thicker. When Ag—Cd systems were heated, only two layers were formed, irrespective of temperature and time of heating. Since this system can give two intermetallic compounds microstructural analysis alone is not sufficient for us to draw conclusions on the nature of the diffusion layers formed.

The results of the microstructural analysis were only approximate, and were later checked by X-ray studies.

c. X-ray studies of diffusion layers. The X-ray study of diffusion layers can be facilitated by using published data on the structure of intermetallic phases.

Natta and Frerri /76/ widely studied the Ag—Cd system, and found that the  $\beta$ -phase has a centered cubic lattice with a parameter of 3.22 Å. The  $\gamma$ -phase has a cubic lattice with 52 atoms per unit cell, and a 9.99 Å lattice parameter, and the  $\epsilon$ -phase has a close-packed hexagonal lattice with  $\frac{c}{a} = 1.58$ .

Westgren /74/ studied the Ag—Zn system, and found  $\beta$ -,  $\gamma$ - and  $\epsilon$ -phases with structures similar to those of the corresponding phases in the Cu—Zn and Ag—Cd systems. Data on the Ag—Zn system are given on page 78. The existence of a  $\gamma$ -phase with a 9.59 Å lattice parameter in the Cu—Cd system had already been noted, and the existence of an  $\epsilon$ -phase was confirmed in this research by X-ray structural analysis. Like the  $\epsilon$ -phases of other systems it has a close-packed hexagonal lattice with  $\frac{c}{a} = 1.58$  and  $a = 2.97$  Å. To study diffusion in Cu—Cd and Ag—Zn systems an iron

target was used with the following wavelengths:  $\lambda k_\alpha = 1.93 \text{ \AA}$  and  $\lambda k_\beta = 1.75 \text{ \AA}$ . For diffusion in Ag—Cd systems, the target was used with the wavelengths:  $\lambda k_\alpha = 1.79 \text{ \AA}$  and  $\lambda k_\beta = 1.53 \text{ \AA}$ . The structures of the layers were determined by comparing the values of  $\sin^2 \theta/2$  obtained in this study with similar values from studies of the  $\beta$ -,  $\gamma$ - and  $\epsilon$ -phases in Ag—Zn, Ag—Cd, and Cu—Cd alloys.

The lattice parameters were calculated from the Bragg formula with the Kurdymov correction for absorption.

From the results the following conclusions can be drawn:

1. Diffusion in Cu—Cd systems leads to the formation of  $\epsilon$ - and  $\gamma$ -phases. As expected from the data of structural analyses, the layer bordering on cadmium is formed at the beginning of the diffusion and is an  $\epsilon$ -phase, and the layer bordering on copper is a  $\gamma$ -phase.

2. Diffusion in Ag—Zn systems produces three phases  $\beta$ ,  $\gamma$ , and  $\epsilon$ , irrespective of whether the zinc is liquid or solid. The order of formation of these phases can be determined by microstructural analysis, and it has already been discussed.

3. The data of X-ray and microstructural analyses indicate that diffusion in Ag—Cd systems produces two phases. The data of the X-ray analysis indicate that these are  $\beta$ - and  $\gamma$ -phases, and therefore the low-melting  $\epsilon$ -phase is not formed in this system.

### § 3. Conclusions

The results of studies on diffusion in Cu—Zn, Ag—Zn, Fe—Zn, Ag—Cd, and Cu—Cd systems indicate that phases of different compositions and structures can be formed.

If the phase first formed is not in a state of equilibrium with the liquid alloy (that is, it is not the phase with the lowest melting point in a given system), as in the case of Cu—Zn and Ag—Cd systems, the mechanism of formation is purely reactive in nature. However, no conclusions can be drawn on the mechanism of formation of low-melting phases ( $\epsilon$ -phase) at the beginning of diffusion. If a solid metal reacts with a liquid, a low-melting phase can be formed as the result of the dissolution of the high-melting metal in the low-melting, or of a direct chemical reaction at the metal interface.

Certain conclusions can be drawn from a study of the microstructure of diffusion layers. It is seen that even if the low-melting phase is formed before, or simultaneously with, other phases, its structure, especially at the boundary with a low-melting metal, can be different from that of other phases. The reactions of iron with zinc (Plate 3) or of iron with copper (Plate 4) produces  $\epsilon$ -phase-layers of a non-uniform width ( $\text{FeZn}_7$  and  $\text{CuCd}_3$ ). Some crystals of this phase deeply penetrate the low-melting metal, and often become detached from the layer and engrained in the bulk of the low-melting metal. Sometimes (particularly in the case of Fe—Zn diffusion) the orientation of these crystals resembles that in the columnar structure formed in the solidification of ingots. This structure of  $\epsilon$ -phases shows that they were formed by normal crystallization from the melt (Zn and Cd) saturated at a given temperature with the higher-melting metal (Fe and Cu).\*

\* As we have already described schematically.

Consequently, the low-melting phase was formed during dissolution. It might also have been formed while the specimen was still in the melt, and have crystallized mainly at the surface of the solid metal. Since some parts of this layer may break away and pass into the melt, after solidification they can be found in the bulk of the low-melting metal.

Such low-melting structures are not always formed as a result of diffusion. For example, in the Ag—Zn system, the  $\epsilon$ -phase found in the diffusion layer soon after the start of diffusion has the same microstructure, uniform width, and sharp boundaries, as the phases obtained by reactive processes, for example, the  $\gamma$ -phase in the Cu—Zn system. It can therefore be assumed that the  $\epsilon$ -phase in the Ag—Zn system was also formed by a direct reaction at the surface.

We should like to point out that the possible formation of "reactive" phases was confirmed by studies on the diffusion in Ag—Cd systems. It was found that the low-melting  $\epsilon$ -phases ( $\text{AgCd}_3$ ) did not appear even after prolonged heating at elevated temperatures, although high-melting  $\gamma$ - and  $\beta$ -phases were formed. The reason for this is that one of these phases was formed during the first moments of reaction, before the melts became saturated with silver. The continuous layer on the liquid-solid interface greatly hampered further dissolution of the high-melting metal, and therefore the  $\epsilon$ -phase could not be formed.

Since it has been found that intermetallic phases can be formed by a reaction, we must find the factor determining the physicochemical nature of these phases. As we have already mentioned (page 77), we assumed that the heat of formation of the phases is very important, at least in some cases.

From recent data on the heat of formation of different intermetallic phases, the probability of our assumption can be confirmed to a certain extent. From different published data the following table on the heat of formation was compiled ( $q$  calories/g-atom):

#### 1. System Cu—Zn

$\beta$ -phase ( $\text{CuZn}$ ) . . . . .	$q = 2.5$
$\gamma$ -phase ( $\text{Cu}_5\text{Zn}_9$ ) . . . . .	$q = 3.2$
$\epsilon$ -phase ( $\text{CuZn}_3$ ) . . . . .	$q = 1.9$

#### 2. System Ag—Zn

$\beta$ -phase ( $\text{AgZn}$ ) . . . . .	$q = 1.6$
$\gamma$ -phase ( $\text{Ag}_2\text{Zn}_3$ ) . . . . .	$q = 1.9$
$\epsilon$ -phase ( $\text{AgZn}_3$ ) . . . . .	$q = 1.2$

#### 3. System Ag—Cd

$\beta$ -phase ( $\text{AgCd}$ ) . . . . .	$q = 1.31$
$\gamma$ -phase ( $\text{Ag}_2\text{Cd}_3$ ) . . . . .	$q = 1.42$
$\epsilon$ -phase ( $\text{AgCd}_3$ ) . . . . .	$q = 1.23$

#### 4. System Cu—Cd

$\gamma$ -phase ( $\text{Cu}_2\text{Cd}_3$ ) . . . . .	$q = 0.6$
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A comparison of these data with the earlier results of studies on reactive diffusion shows that the heat of formation of phases greatly influences the sequence of their formation during reactive diffusion.

Thus, in the system the first phase formed is always the  $\gamma$ -phase ( $\text{Cu}_5\text{Zn}_8$ ), which has the highest heat of formation in this system, even greater than the heat of formation of the  $\epsilon$ -phase ( $\text{CuZn}_3$ ) which according to the conditions of equilibrium should be formed during the first stage of the process. In the Ag—Cd system, the  $\epsilon$ -phase, with the lowest heat of formation, is not formed at all. For the Cu—Cd system we have data on the heat of formation of the  $\gamma$ -phase only, and therefore we cannot draw any conclusions on the influence of the heat of formation on the production of a certain phase during the first stage of reactive diffusion in this system. However, the very low heat of formation of the  $\gamma$ -phase in the Cu—Cd system indicates that the heat of formation of the  $\epsilon$ -phase will not be lower than that of the  $\gamma$ -phase, which may explain why the  $\epsilon$ -phase is the first to form in this system.

The above conclusion on the role of the heat of formation is somewhat contradicted by the data on diffusion in Ag—Zn systems, in which all three phases are formed simultaneously, although the heat of formation of the  $\gamma$ -phase ( $\text{Ag}_2\text{Zn}_3$ ) is somewhat higher than that of other phases. Therefore, it can be assumed that the heat of formation, which certainly influences reactive diffusion, is not the only factor determining the nature of the phase formed at the beginning of diffusion.

The data indicate that the influence of the heat of formation is appreciable if this heat has a high absolute value and greatly exceeds the heats of formation of other phases in the same system. If, however, the heat of formation has a low absolute value (as in the Cu—Cd system), or it differs little from the heat of formation of other phases in the system (as in the Ag—Zn system), its influence on reactive diffusion is small.

Thus, the heat of formation should be regarded as only one of the factors influencing the reactive formation of phases.

On the other hand, the physicochemical nature and the structure of the "reactive" phase probably depend on external conditions of the process also, especially the temperature. It also seems probably that reactive diffusion and the nature of the phases produced are influenced by the state and structure of the surface of the high-melting metal on which new phases are formed.

It is not very possible to give any general indication of the nature of the phases formed by reactive diffusion at the metal interfaces since this is influenced by numerous factors. We can only maintain that we are fairly certain that the heat of formation of phases has a great, and sometimes decisive, influence. The influence of temperature, the state and structure of the surface, impurities, etc. should be fully considered in each particular case.

## Chapter II

### LAWS GOVERNING THE GROWTH OF DIFFUSION LAYERS DURING REACTIVE DIFFUSION

To study the reactive diffusion of metals, not only the physicochemical nature, composition and structure of the phases formed must be determined, but also the rates of growth of these phases. It is interesting to compare the growth rates and the parameters which determine them with those for atomic diffusion of one metal in the lattice of another.

There are a few published data indicating that the diffusion in intermetallic phases is faster than in pure metals. However, there are no systematic studies on this subject.

The growth rate of intermetallic phases during the diffusion of different metals is of great practical importance. The intermediate layers formed in protective metal coatings (zinc, tin, calorizing, nitriding, etc.) usually consist of one or more intermetallic phases, and the properties of these phases (mainly mechanical) are highly influenced by their structure and thickness.

The laws governing the rate of atomic diffusion (during the formation of slightly concentrated solutions in the lattice of the solvent metal) cannot be directly applied here. But sometimes under certain limiting conditions this law holds.

Such cases have been discussed by Tamman and Rocha /72/, who described a method for determining diffusion coefficients. If diffusion produces one or several intermetallic compounds in the form of separate layers, the layers start to grow at different rates. The diffusion coefficient for each layer can be found if there is a linear drop in concentration in each layer. The difference between the concentrations on the (opposite) interfaces must remain constant at a given temperature:  $\Delta C = \text{constant}$ .

Under these conditions we can write the formula:

$$dn = -Dq \frac{\Delta C}{y} dt, \quad (1)$$

where  $dn$  is the amount of substance diffusing in  $dt$  through a section  $q$ ;  $\frac{\Delta C}{y}$  is the concentration drop along a layer of thickness  $y$ ; and  $D$  is the diffusion coefficient.

On the other hand, if the concentration at the layer boundary is constant, we can assume that the thickness increase is proportional to the amount of diffused substance, i. e.,

$$dn = aq dy, \quad (2)$$

where  $dy$  is the increase in the thickness of the layer; and  $a$  is a proportionality factor with the dimensions of the concentration of the substance.

If we compare the right-hand sides of formulas (1) and (2), we obtain:

$$D \frac{\Delta C}{y} dt = a dy \quad \text{or} \quad D \frac{\Delta C}{a} dt = y dy,$$

hence

$$D \frac{\Delta C}{a} t = \frac{y^2}{2}.$$

We assume that  $D \frac{\Delta C}{a} = p = \text{const}$ , since at this temperature  $D = \text{const}$ ,  $\Delta C = \text{const}$  and  $a = \text{const}$ , and finally obtain

$$y^2 = 2pt, \quad (3)$$

which means that at a given temperature the growth of the layer is governed by a parabolic law.

The parameter  $2p$  of the parabola characterizes the growth rate of the layer. It is proportional to the diffusion coefficient and is expressed in the same dimensions.

A similar dependence was obtained by Frenkel' and Sergeev /77/, who studied this problem more widely statistically.

An experimental study of a number of systems by Tamman and Rocha, and Weiss /68/ showed that the parabolic law of the growth of phases holds in many cases.

The study of the dissolution of high-melting metals in low-melting is also complicated because the growth of the layer is accompanied by its dissolution in the liquid metal. Thus, the concentration on the boundary of the growing layer changes, which leads to deviations from the parabolic law. This exerts a certain influence, although a small one, if the layer being studied is not in direct contact with the liquid metal. The parabolic law is true only if the liquid metal is saturated with the dissolved substance, or if the solubility of the high-melting metal in the low-melting one is low (for example, as the result of great difference in the melting points).

Measurement of the temperature dependence of the diffusion coefficient for processes in which intermetallic compounds are formed is the simplest and most accurate method for studying the kinetics of reactive diffusion.

The temperature dependence of the growth of diffusion layers has until now been calculated mainly from the formulas:  $x = BT^m$  or  $x = BT^{m-1}$ , where  $x$  is the thickness of the layer;  $T$  is the temperature and  $B$  and  $m$  are coefficients.

Although these formulas often satisfy the results of experiments, they are purely empirical, and are not related to the fundamental constants which determine the mobility of atoms, including the heat of activation  $Q$ . On the other hand, the value of  $p$  in formula (3) which determines the growth of the diffusion layer is proportional to the diffusion coefficient, and therefore for each of the phases formed we can expect an exponential dependence of this parameter on temperature, as in the case of ordinary atomic diffusion. Since the differences in concentration within the same layer are small, the value of  $2p$  can be regarded as constant, and dependent on temperature only.



Thus, we must determine how much the temperature dependence of the growth of the layer is described by equation:

$$2p \simeq D = Ae^{-Q/RT},$$

and how great is the heat of activation (loosening) for different metal systems.

Bugakov and Gluskin /70/ studied the kinetics of the growth of diffusion layers in the same systems previously used to study the nature of the diffusion phases (Cu—Zn, Fe—Zn, Ag—Zn, Ag—Cd, and Cu—Cd).

The methods were fundamentally the same as described above. In some cases (including diffusion in Cu—Zn systems) the liquid metal was saturated with the high-melting metal to avoid the influence of dissolution at the beginning of the experiment. The constancy of the thickness of the layers at a given temperature and holding time was checked by repeating the experiment under the same conditions. Usually, the thicknesses measured under a microscope at a magnification of 105 were found to be the same.

a) Kinetics of the growth of layers during diffusion in Cu—Zn and Fe—Zn systems. During research on interdiffusion in Cu—Zn and Fe—Zn systems, we studied mainly the growth of the  $\gamma$ -layer, since this phase produced the most distinctive interface, and was formed at all temperatures over the range investigated. This phase conforms best to the condition for applying the parabolic law (constancy of composition on the boundaries), since it does not come into direct contact with the liquid metal. Thus, even if this solution has a certain influence, this will be only at short holding times during diffusion in Cu—Zn systems when no  $\epsilon$ -phase was formed.

The other condition (a linear drop in concentration within the layer) is important only in Cu—Zn systems in which the  $\gamma$ -phase exists over a fairly wide range of concentrations. As we have already mentioned (p. 75 and Figure 24), this condition is fulfilled here quite satisfactorily.

The thickness of layers of the  $\gamma$ -phases of Cu—Zn and Fe—Zn systems were measured at different temperatures and holding times in the solid and liquid states of the low-melting metal.

The results are plotted in the  $y^2-t$  coordinates, where  $y$  is the thickness of the layer, in microns, and  $t$  is the duration of diffusion in hours.

Figures 25 and 26\* show some of the curves obtained, which indicate that there is always a straight line dependence of  $y^2$  on  $t$ , or in other words that the parabolic law of growth  $y^2=2pt$  holds. The mean parameter  $2p$  for each parabola is determined as the slope of the corresponding straight line with the axis  $t$ . As we have already mentioned, this parameter is proportional to the diffusion coefficient.\*\* If we know the value of  $2p$  at various temperatures, we can determine the temperature dependence of the diffusion coefficient.

Since it seemed probable that in our systems, as in simple solid solutions, there is an exponential temperature dependence of the diffusion coefficient:

( $2p \simeq D = Ae^{-Q/RT}$ ), the temperature curves were plotted in  $\frac{1}{T} - \ln 2p$  coordinates.

\* The numerical values are tabulated in the work of V. Bugakov and D. Gluskin.

\*\* Below we shall call this the coefficient of diffusion.

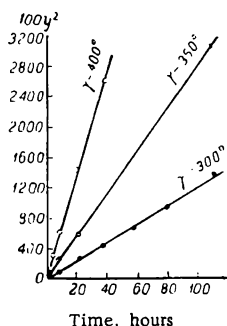


FIGURE 25. Growth of Cu-Zn diffusion layers.

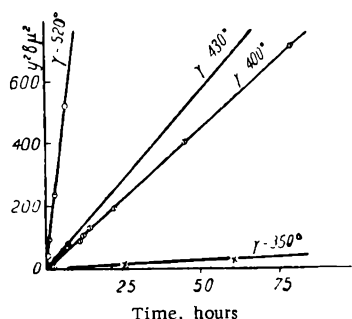


FIGURE 26. Growth of Fe-Zn diffusion layers.

Figure 27 shows the temperature dependence of the diffusion coefficients for  $\gamma$ -phases of the Cu-Zn and Fe-Zn systems. The numerical values corresponding to these curves are given in Table 40.

TABLE 40. Temperature dependence of the diffusion coefficient for  $\gamma$ -phases

Temperature, °C	$\frac{1}{T}$	Cu-Zn		Fe-Zn	
		$2p$	$\ln 2p$	$2p$	$\ln 2p$
600	$1.14 \cdot 10^{-3}$	$108.3 \cdot 10^8$	11.58	—	—
520	$1.25 \cdot 10^{-3}$	$81 \cdot 10^8$	11.3	$77 \cdot 10^2$	8.94
420	$1.43 \cdot 10^{-3}$	$24.2 \cdot 10^8$	10.65	$13 \cdot 10^2$	7.16
400	$1.49 \cdot 10^{-3}$	$75 \cdot 10^2$	8.9	$9 \cdot 10^2$	6.67
350	$1.63 \cdot 10^{-3}$	$28.4 \cdot 10^2$	7.9	$0.43 \cdot 10^2$	3.75
300	$1.75 \cdot 10^{-3}$	$12 \cdot 10^2$	7.1	—	—
225	$2 \cdot 10^{-3}$	$2 \cdot 10^2$	5.3	—	—
150	$2.3 \cdot 10^{-3}$	$0.38 \cdot 10^2$	3.6	—	—

The straight line dependence of  $\ln 2p$  on  $1/T$  for diffusion in Cu-Zn and Fe-Zn systems confirms the assumption on the exponential nature of the temperature dependence of the diffusion coefficient.

All points in Figure 27 for Cu-Zn and Fe-Zn systems lie on the same straight line.

These straight lines have no bends, because the low-melting metal (Zn) passes from the solid state to the liquid, which indicates that the heat of loosening  $Q$  (slope of the temperature curve) is not influenced by the state of the low-melting metal.

The heat of loosening found from the temperature curve is as follows:

For diffusion in Cu-Zn . . . . .  $Q = 15,200 \text{ cal/g}$ ,

For diffusion in Fe-Zn . . . . .  $Q = 17,680 \text{ cal/g}$ .

b) Kinetics of the growth of layers during diffusion in Ag-Zn, Ag-Cd, and Cu-Cd systems. During the research on diffusion in these systems, we

studied the growth of all phases formed, including the  $\epsilon$ -phases in the Cu—Cd and Ag—Zn systems. In the Ag—Zn system the  $\epsilon$ -phase had the same distinct boundaries and the same uniform width as other phases, so that it was possible to determine its width with great accuracy. In the Cu—Cd system, the  $\epsilon$ -phase had no such distinct boundaries, especially at the side of the low-melting metal. Its width differed somewhat at different points. To obtain more or less accurate results, we had to make several measurements and find the mean values. We should expect that the concentration of the  $\epsilon$ -phase at the boundary with the low-melting metal will also vary, but as the liquid metal (Cd) becomes saturated with the high-melting metal (Cu) during the process, these changes are small.

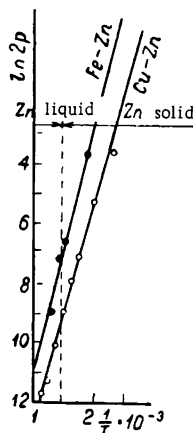


FIGURE 27. Growth of Cu—Zn and Fe—Zn diffusion layers.

The results of measurements of the thickness for all the systems plotted in  $y^2-t$  coordinates are shown in Figures 28—32. It can be seen that there is always a straight-line relationship between the square of the thickness and the diffusion time, which means that the parabolic law  $y^2 = 2pt$  holds for the rate of growth of the layer.

The curve representing diffusion in Cu—Cd systems at 240°C differs from other curves in the existence of a bend. At the beginning of the diffusion the  $\epsilon$ -phase only is formed and grows. However, after a certain time a  $\gamma$ -phase appears, which changes the boundary conditions of the  $\epsilon$ -phase, and thus a bend appears on the curve.

Figures 33—35 show the the temperature dependence of the diffusion coefficient in the  $\ln 2p$  and  $\frac{1}{T}$  coordinates. They indicate that in these systems, as in the Cu—Zn and Fe—Zn systems, there is an exponential dependence of the diffusion coefficient on temperature. The slopes of the straight lines determine the heat of loosening for all phases of the systems studied. The available data are given in Table 40.

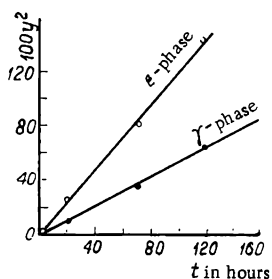


FIGURE 28. Growth of Cu-Cd diffusion layers.

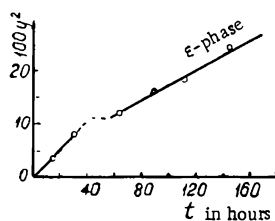


FIGURE 29. Growth of Cu-Cd diffusion layers.

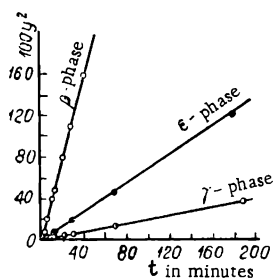


FIGURE 30. Growth of Ag-Zn diffusion layers.

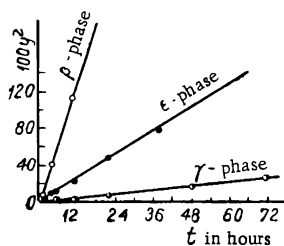


FIGURE 31. Growth of Ag-Zn diffusion layers.

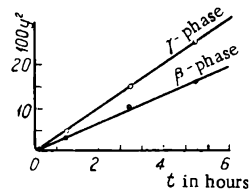


FIGURE 32. Growth of Ag-Cd diffusion layers.

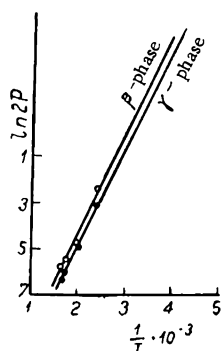


FIGURE 33. Growth of Ag-Cd diffusion layers.

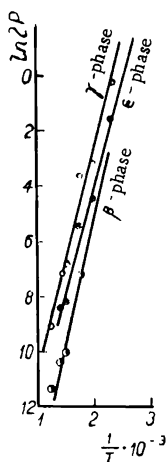


FIGURE 34. Growth of Ag-Zn diffusion layers.

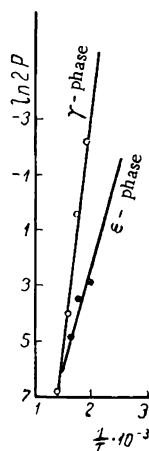


FIGURE 35. Growth of Cu-Cd diffusion layers.

Conclusions on the kinetics of the growth of phases formed by reactive diffusion. From the experiments described in this chapter some conclusions can be drawn on the laws governing the growth of intermetallic layers formed as a result of diffusion.

The most important of these conclusions are the following.

1) The rate of growth of layers, that is increase in their thickness, is governed by a parabolic law theoretically derived by Tamman and Rocha, and Frenkel and Sergeev.

It should be pointed out that the applicability of this law was studied at a certain moment after the start of diffusion only. For example, in Cu—Zn systems the thickness of the  $\gamma$ -layer was measured one minute after the start of the process, and in Fe—Zn systems five minutes after. The first measurements carried out a short time after diffusion started showed that the diffusion layers had reached a measurable thickness. Obviously, it was impossible to determine the course of growth at the very beginning of diffusion. From the data obtained we can only conclude that in certain systems the initial rate of formation of intermetallic phases is more rapid than their further growth governed by a parabolic law.

Therefore, we must differentiate between the following two stages of reactive diffusion: 1) formation of an intermetallic phase by a surface reaction; and 2) growth of this phase as a result of diffusion.

These stages proceed at different rates. For the first reactive stage this will be the rate of the surface reaction, which is apparently determined by the conditions under which these reactions take place, in particular, temperature, heat of formation, structure of basis metal, etc. The rate of the second stage of the process is determined by the diffusion coefficient, which as we have seen can be found from the law governing the growth of the layer.

2. It has been experimentally found that the exponential dependence of the diffusion coefficient (parameter  $p$ ) on temperature is always retained. The direction of the temperature curve remains the same, irrespective of whether the low-melting-metal is liquid or solid. This is only natural, since the growth of the intermetallic layers is always due to diffusion in the solid whatever the state of the low-melting metal. The physical state of the metal is important during the initial stage of interaction only, when the intermetallic phase starts to be formed.

3) From the curves showing the temperature dependence of the diffusion coefficient the heat of loosening  $Q$  can be found for each of the phases studied (Table 41).

TABLE 41.

Diffusing metals	Heat of loosening $Q$ for phases:			
	$\alpha$	$\beta$	$\gamma$	$\epsilon$
Ag—Zn . . .	$23 \cdot 10^3$	$18 \cdot 10^3$	$15.5 \cdot 10^3$	$15 \cdot 10^3$
Cu—Zn . . .	$38 \cdot 10^3$	—	$15.2 \cdot 10^3$	—
Fe—Zn . . .	—	—	$17.7 \cdot 10^3$	—
Ag—Cd . . .	$20 \cdot 10^3$	$9.4 \cdot 10^3$	$9 \cdot 10^3$	—
Cu—Cd . . .	—	—	$33.2 \cdot 10^3$	$15.2 \cdot 10^3$

For comparison, Table 41 also gives some data on atomic diffusion in lattices of the high-melting metal in  $\alpha$ -solid solutions.

The data on the diffusion of cadmium and zinc in the lattices of silver were taken from /51/, and the data on the diffusion of zinc in copper from the paper of Mehl and Rhines.

Table 41 shows that the heat of loosening during diffusion in intermetallic phases is always lower than in  $\alpha$ -solid solutions of the high-melting metals. This indicates that the heat of loosening decreases with increase in concentration of the low-melting metal. Therefore, the  $\epsilon$ -phases have a lower  $Q$  than the  $\alpha$ -solid solutions (this is particularly noticeable in diffusion in Ag-Zn and Ag-Cd systems).

The decrease in  $Q$  is mainly due to the decrease in the melting point of the corresponding phases, and as expected, the phase with the lowest melting point has the smallest heat of loosening.

Experiments show that the  $\gamma$ -phases of the Ag-Zn, Cu-Zn, and Fe-Zn systems have very close heats of loosening ( $Q$ ). The small divergencies are due to the differences in the melting points. These results are understandable since the  $\gamma$ -phases of these systems have not only similar crystallographic structures, but also the same electron density (according to Hume-Rothery the number of electrons per atom is 21/13).

There are appreciable differences between the heats of loosening of  $\gamma$ -phases in Ag-Cd and Cu-Cd systems. The heat of loosening of the first system is much higher than that of the three above-mentioned systems, but the heat of loosening of the second is much lower. Unfortunately, we are still unable to explain these differences.

In conclusion, we should like to mention that the heat of loosening of intermetallic phases remains within the limits obtained for atomic diffusion.

We should also add that for atomic diffusion the diffusion coefficients and the values of  $Q$  are partly influenced by the concentration, and can vary considerably as the result of the widely varying compositions of the solutions. The values of  $D$  and  $Q$  for diffusion in intermetallic phases are more stable and reliable, since the compositions of the intermetallic phases are more constant.

### *Chapter III*

#### *REACTION OF IRON WITH LIQUID ZINC (THEORY OF ZINC COATING OF IRON)*

Theoretical and practical importance of the reaction  
between iron and liquid zinc

In the previous chapter we discussed the nature of the phases formed by reactive diffusion, and the laws governing their growth as a function of time and temperature. It was found that during the reaction between a liquid low-melting metal and a solid high-melting one the sequence of formation of intermetallic phases does not always correspond to the equilibrium conditions on the interface. Sometimes the composition and structure of the phase formed at the beginning of the reaction are not the same as those of the phase with the lowest-melting point in the system. Therefore, we assumed that metallic phases can be formed during reactive diffusion in one of two ways: as the result of the dissolution of the high-melting metal in the melt (equilibrium), or by a direct chemical reaction at the interface. In the first case, the phase with the lowest melting point forms first, which corresponds to equilibrium conditions, and in the second case, a phase for which the reaction conditions at the interface are most favorable is formed first.

It can be assumed that the reaction between the solid high-melting metal and the liquid low-melting involves simultaneous processes: dissolution and chemical reaction on the interface. Each of these can produce various phases, and therefore the final structure of the diffusion layer will depend on the relative rates of these two processes. If the rate of the reaction on the surface is much higher than the rate of dissolution, an intermediate high-melting intermetallic phase will be formed on the interface of the two metals. This phase will hinder the supply of solid metal to the melt, and therefore the formation of the low-melting phase produced as a result of dissolution. On the other hand, the ratio between the rates of dissolution and chemical reaction on the surface should be influenced by a number of factors, including the temperature at which the reaction proceeds. A change in temperature can alter the rate of the above two processes, and thus the final structure of the diffusion layers. The state and structure of the surface of the solid high-melting metal, the presence of impurities in the melt, etc., also have a certain influence.

In this chapter we shall discuss the reaction between high-melting metals and liquid, and also a number of factors, including temperature, which influence this reaction.

For our studies we chose the Fe—Zn system, which we have already mentioned in our discussion on the research on the reaction between iron and liquid zinc. However, this work was not complete, and was confined to a study of the kinetics of growth of the  $\text{Fe}_5\text{Zn}_{21}$  phase, and the conditions of dissolution were not considered.

The reaction between iron and zinc is of great theoretical interest, and many published data (which we shall discuss later) indicate that it may lead to the formation of very differing structures, depending on the conditions. However, the authors of these data came to no definite conclusion on the reasons for such variation. Moreover, the reactions by which the individual diffusion layers are formed are still not clear. Therefore we decided to carry out a systematic study of this system based on the principles of reactive diffusion of metals that we discussed above.

The reaction between iron and zinc is also of great practical value, since it is the basis of the important process of hot-dip zinc coating of iron. In many methods for producing protective coatings, zinc is very important, because it can be easily and inexpensively applied and gives a layer resistant to corrosion by different media.

Today, there are numerous methods for applying zinc to the surface of iron.

The most ancient and widely used method is hot-dip coating, which has been used in industry for about 200 years. Competing with this method is electrolytic zinc plating, which has displaced the hot-dip process in some branches of industry. Nevertheless, statistical data show that the hot-dip method is still predominant, and according to Bablik, 50—60% of the zinc mined today is used for hot-dip coating.

The advantages of the different methods of zinc-coating have been widely discussed, but many research workers prefer the hot-dip method, at least for coating some products. Hot-dip coating is clearly advantageous if thick layers are required in service, as these can be more readily obtained by dipping in liquid zinc.

Although the hot-dip method is widely used, the theory of this process has not yet been fully developed, and it cannot always explain the phenomena encountered in practice.

The most important properties of zinc coatings are their good corrosion resistance and high mechanical strength. The corrosion resistance of zinc coatings is determined mainly by their thickness, particularly by that of the upper layer of pure zinc. The lower layers contain intermetallic Zn—Fe compounds, and are less important.

The mechanical strength of the layer and its adhesion to the basis metal are very important in thick deposits.

Usually, with increase in the thickness of the deposit the mechanical properties deteriorate. This is because the increase in thickness obtained in ordinary zinc-coating processes involves an increase in the thickness of the intermetallic layers (formed by a reaction). These are brittle and adhere poorly to the basis metal.

Hence, to produce high-quality deposits, it is essential that the layer of pure zinc should be as thick as possible and the intermetallic layer reduced to a minimum.

To satisfy these conditions, and give a theoretical proof of the existing experimental data, the kinetics of the reaction between iron and zinc must be studied.



Thus, a solution of the theoretical problem discussed here will help to determine the conditions for the production of strong zinc deposits, and this part of our work should be regarded as an attempt to give some of the theoretical principles of the zinc-coating of iron.

## A. REVIEW OF LITERATURE DATA

### § 1. Phase diagrams of Fe—Zn alloys, and the structure of different phases in these systems

Vegesack /79/, Raydt and Tammann /80/, and Peirce /81/, were the first to study Fe—Zn phase diagrams. Their results are very similar, and differ only in detail. One of Peirce's phase diagrams is shown in Figure 36.

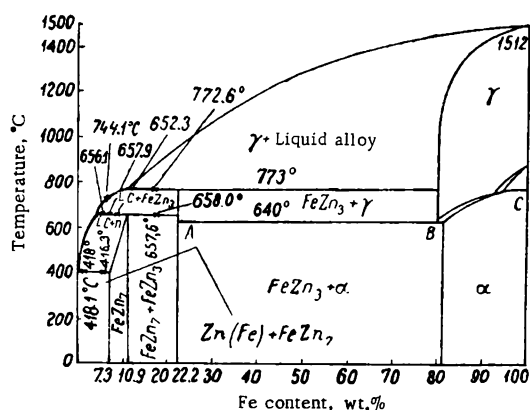


FIGURE 36. Fe—Zn phase diagram (after Peirce).

As can be seen from this phase diagram, the region adjacent to Fe contains an  $\alpha$ -solid solution of zinc in iron with a maximum concentration of 20% Zn. At elevated temperatures the  $\alpha$ -solid solution is transformed into a  $\gamma$ -solid solution of Zn in Fe with the same region of solubility.

The Zn-rich region contains two intermetallic phases ( $\text{FeZn}_3$  and  $\text{FeZn}_7$ ). The first is formed by a peritectic reaction at about 775°C, and contains about 22% Fe. According to the diagram it has no region of solubility.

The  $\text{FeZn}_7$  phase is also formed by a peritectic transformation at about 660°C (658—666°C according to various sources), but it has a certain region of solubility between 7 and 11% Fe. The phase diagram does not indicate the existence of a solid solution in the zinc lattice, and the solubility of iron in solid zinc is negligible, if it exists at all.

The phase diagram shows that there is a eutectic ( $\text{FeZn}_7 + \text{Zn}$ ) in the region between the  $\text{FeZn}_7$  phase and pure Zn.

The intermediate part of the diagram has heterogenous regions containing the ( $\alpha$  +  $\text{FeZn}_3$ ) and ( $\text{FeZn}_3$  +  $\text{FeZn}_7$ ) phases.

This diagram is very similar to the Fe—Zn phase diagram obtained at the beginning of this century.

Appreciable changes have been only recently introduced into this phase diagram, mainly by Schramm /82/. His phase diagram (Figure 37) is based on different physicochemical studies.

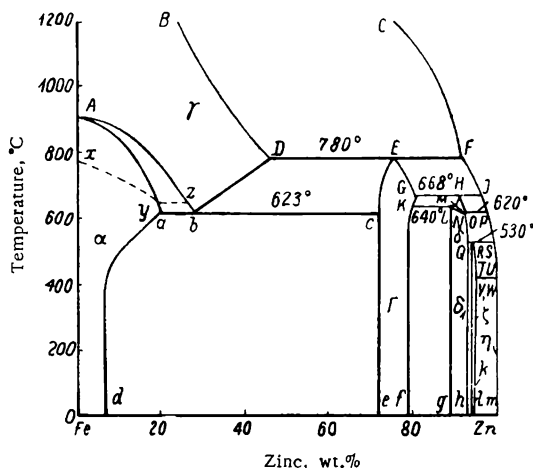


FIGURE 37. Fe—Zn phase diagram (after Schramm).

The new phase diagram indicates the existence of not only the previously found two intermetallic compounds,  $\text{FeZn}_3$  and  $\text{FeZn}_7$ , but also of another compound richer in zinc which contains between 6.0 and 6.2% Fe.

Thus, Schramm found the following intermetallic phases in the Fe—Zn system:

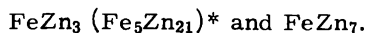
$\Gamma$ -phase with a composition close to  $\text{Fe}_5\text{Zn}_{21}$ , which exists at room temperature in the region of 20—27% Fe;

$\delta$  - phase in the region of 7—11 % Fe;

$\xi$  - phase in the region of 6—6.2 % Fe.

Besides these three phases, an  $\alpha$ -solid solution of Zn in iron, and an  $\eta$ -solution, which is almost pure zinc, can also exist at room temperature.

The crystallographic structure of intermetallic phases in the Fe—Zn system has been studied by different authors by X-ray structural analysis methods. One of the first studies by Osawa and Ogawa we have already mentioned. These authors found only two intermetallic compounds



Further studies generally confirmed the data of Osawa and Ogawa on the intermetallic  $\text{Fe}_5\text{Zn}_{21}$  compounds. According to the more recent and

\* Henceforth, we shall assign the formula  $\text{Fe}_5\text{Zn}_{21}$  to this phase, as it is more correct (see above).

complete studies of Schramm, this phase ( $\Gamma$ -phase of Schramm) has a cubic lattice with 52 atoms in the unit cell, and a parameter of  $8.95-8.93 \text{ \AA}$  (according to Osawa and Ogawa this lattice parameter is equal to  $8.89-8.93 \text{ \AA}$ ).

On the other hand, the data of Osawa and Ogawa on the structure of the second  $\text{FeZn}_7$  phase have not been confirmed by later authors.

From X-ray studies of this phase ( $\delta$ -phase of Schramm), Schramm concluded that the  $\delta$ -phase has a lattice which is more complex than the close-packed hexagonal lattice.

No accurate description of the structure of the  $\delta$ -phase was given by Schramm.

The crystal structure of the  $\delta$ -phase has recently been studied by Bablik, Götzl, and Halla /83/, who used the Debye rotating crystal and Weissenberg methods. These authors found that the  $\delta$ -phase has a hexagonal lattice with the following dimensions of the unit cell:  $a = 12.8 \text{ \AA}$ ,  $c = 57.6 \text{ \AA}$ . The cell contains  $550 \pm 8$  atoms (volume of unit cell  $V = 8173 \text{ \AA}^3$ ).

This lattice belongs to the  $D_{6h}^4$  space group.

We have already mentioned that the  $\text{Fe}-\text{Zn}$  phase diagrams constructed recently by Schramm include not only the above two phases but also another intermetallic phase ( $\xi$ -phase), which is richest in zinc. The existence of such a low-melting phase had already been suspected. Thus, in 1921 Lehman /84/ studied the magnetic properties of  $\text{Fe}-\text{Zn}$  alloys, and found a maximum on the curve of magnetic saturation corresponding to an alloy with 7.3% Fe. He concluded that the  $\text{Fe}-\text{Zn}$  phase diagrams known at that time were incomplete.

Somewhat later, in 1925, a phase with a composition  $\text{FeZn}_{10}$  was found by Schueler /85/ in heat-treated zinc coatings. Schramm /82/ studied the  $\xi$ -phases by X-ray thermal, magnetic, and microstructural analyses. By X-ray methods he studied alloys containing 6.0 and 6.5% Fe after different heat-treatment processes. Hence, he concluded that the  $\xi$ -phase is formed by a peritectic reaction  $\delta + \text{L} \rightarrow \xi$  at  $530^\circ\text{C}$ , and that this phase is stable at room temperature.

Thermal and magnetic analyses gave no clear indication of the formation of this phase. A microstructural study with a special reagent confirmed that a  $\xi$ -phase does exist, and that its appearance is different from that of the  $\delta$ - and  $\Gamma$ -phases. The author, however, believes that both the physical and chemical properties of  $\delta$ - and  $\xi$ -phases are very similar, and that their separation by etching is rather difficult.

In a later study, Schramm found that the  $\xi$ -phase has a lattice similar to that of the  $\delta$ -phase.

However, he did not determine its crystal structure more accurately.

Later, Halla, Weil, and Götzl /88/ found that the  $\xi$ -phase has a monoclinic lattice with the following parameters:  $a = 13.65 \text{ \AA}$ ,  $b = 7.61 \text{ \AA}$ , and  $c = 5.06 \text{ \AA}$ , and  $\beta = 178^\circ 44'$  (space group  $C_{2h}^2$ ). According to these authors, the  $\xi$ -phase has the formula  $\text{FeZn}_{13}$ , and contains from 6 to 6.2% Fe.

## §2. Published data on the structure of zinc coatings and the reaction of iron with liquid zinc

The discovery of a new  $\xi$ -phase in the Fe—Zn system and the changes made in the phase diagram complicated the problem of the structure of zinc coating.

Until 1936—1937 it was believed that this system had only two phases formed by the reaction of iron with liquid zinc: an  $\text{Fe}_5\text{Zn}_{21}$  ( $\text{FeZn}_3$ ,  $\text{Fe}_3\text{Zn}_9$ ) compound, or the  $\Gamma$ -phase according to the recent designation of Schramm, and an  $\text{FeZn}_7$  compound ( $\delta$ -phase). The numerous studies on the process of zinc coating of iron, summarized by Bablik /86/, Roudon /87/, and others have shown that two layers corresponding to the  $\Gamma$ - and  $\delta$ -phases have already formed on the surface of iron after one minute of hot-dip zinc coating. There are also indications that one of these layers, usually the  $\Gamma$ -phase, is not formed in the coating.

Diffusion layers of such a composition have been found after the prolonged immersion of iron in liquid zinc. The early research of Grubitsch /89/, Sheil /90/ and co-workers, and others indicate that only two inter-metallic layers, corresponding to the  $\Gamma$ - and  $\delta$ -phases, are formed in the range of 450—500°C. We obtained similar results /70/. An X-ray analysis of diffusion layers formed by prolonged immersion of iron in zinc at 430°C revealed the presence of two phases corresponding to  $\text{Fe}_5\text{Zn}_{21}$  and  $\text{FeZn}_7$  compounds. The microstructure of diffusion layers confirms these results. Figure 26 shows the structure of coatings obtained at 430°C; these contain only two layers. There is no doubt that the layer next to iron consists of the  $\Gamma$ -phase ( $\text{Fe}_5\text{Zn}_{21}$ ), and the other layer is a  $\delta$ -phase ( $\text{FeZn}_7$ ).

The results of research during the last years indicate the existence of an  $\xi$ -phase. In one of his latest works Bablik /91/ shows that the  $\delta$ - and  $\xi$ -phases comprise the major part of the coatings. To explain the formation of structures at different temperatures, he points out that the reaction  $\delta + \text{L} \rightarrow \xi$  does not take place at 530°C, as indicated by Schramm, but at  $495 \pm 5^\circ\text{C}$ . Grubitsch and Brückner /92/ studied the structure of the coating from the new phase diagram constructed by Schramm and concluded that zinc coating at up to 485°C for 60 minutes produces all three phases, and that the  $T$ -layer is the thinnest. Similar results were obtained by Scheil and Würst /93/, who found that coatings formed at 450°C contain all three phases.

The above authors could not confirm the existence of the  $\xi$ -phase by X-ray structural analysis, and assumed that it existed from the results of a microstructural analysis.

Most authors agree that only a  $\delta$ -phase is formed at 450—520°C, and that both  $\Gamma$ - and  $\delta$ -phases are produced at temperatures above 520°C.

There are controversial data on the  $\xi$ -phase described here. Its existence on the phase diagrams of Fe—Zn alloys is fairly certain, but the presence of the  $\xi$ -phase in the structure of zinc coatings on iron as an individual layer clearly separated from other diffusion layers is not so probable. Also, a layer such as the  $\xi$ -phase has never been found in earlier studies on the zinc coating of iron, and no such layer has been found in the more recent research of, for example, Thalemann /94/ and ourselves /70/.

Scheil and Würst do not give adequate proof of the existence of this phase as an individual diffusion layer /95/. Thus, Plate 5 (see Appendix)

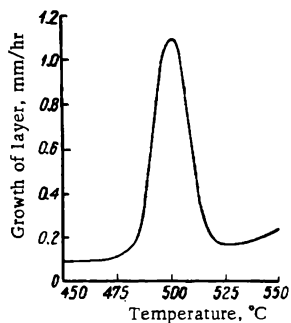


FIGURE 38. Dependence of the rate of dissolution on temperature.

taken from the paper of Scheil and Würst clearly shows two types of crystals, dark ones clearly oriented perpendicular to the basis of the layer and bright ones of a more or less regular shape distributed in the background of the dark crystals. The dark crystals are assumed to be a  $\delta$ -phase, and the light, an  $\xi$ -phase.

Irrespective of whether the nature of these crystals is given correctly or not, it is important that there is no boundary between them.

The X-ray studies of Schramm showed that the  $\delta$ - and  $\xi$ -phases grow at a high rate in one preferred direction.

All these data indicate that if the  $\xi$ -phase exists in the coating it does not form a separate layer and is not separated by a boundary from the  $\delta_1$ -layer. This is all the more probable as

the structure of the  $\xi$ -phase is very similar to that of the  $\delta_1$ -phase.

We shall now discuss the kinetics of the reaction of iron with liquid zinc. This problem has been studied by two methods: by determining the rate of dissolution of iron in liquid zinc (by measuring the weight loss of iron specimens) at different temperatures, and by studying the growth of diffusion layers with time at different temperatures /96, 89, 90, 95/. The most important result of these studies is that they confirmed the existence of a maximum rate of dissolution of iron in liquid zinc over a certain temperature range.

The curves showing the dependence of the rate of dissolution (weight loss per unit time) on temperature are similar to those in Figure 38, which were obtained by Scheil and Würst /93/.

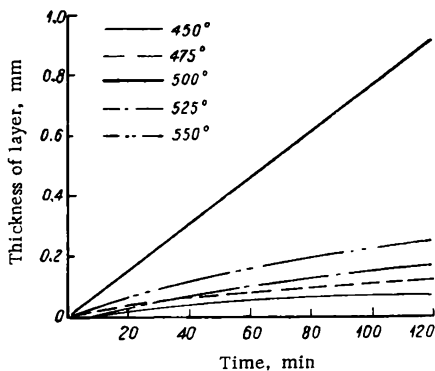


FIGURE 39. Growth rate of diffusion layers.

Different authors give different temperatures for this maximum, but all the data lie within the range of 480–520°C. The temperature curve is

similar to those representing the dependence of the growth of diffusion layers on time at a constant temperature. Figure 39 shows the curves of Scheil and Würst. An analysis of these curves shows that at temperatures below 480°C the layer grows rather slowly, and that this growth is governed by a parabolic law. Between 480 and 520°C (Figure 39, at 500°C) the layer grows rapidly and the curve becomes linear. Finally, above 520°C the growth is again governed by a parabolic law, and is appreciably slowed down. This growth of diffusion layers indicates the existence of two types of reaction between iron and liquid zinc. The reaction governed by a parabolic law of growth was designated as the reaction of the first type, and the linear growth of the layer is due to a reaction of the second type.

Tungel, Scheil, and Shtengoff, studied a large number of steels of various compositions, and concluded that the temperature curve with a maximum solubility is not characteristic of all steels, but only of those which give a smooth solubility curve.

The same authors point out that the type of reaction is related to the structure of the zinc coating. The reaction of the second type produces no  $\Gamma$ -phase ( $\text{Fe}_5\text{Zn}_{21}$ ), but this phase is formed by the reaction of the first type. This conclusion was confirmed by the X-ray studies of Scheil and Würst. These authors believe that the absence of the  $\Gamma$ -phase is due to the sharp increase in the rate of dissolution of iron during the reaction of the second type.

But not one of these authors was able to indicate the conditions necessary for these two types of reaction, or how these reactions are influenced by the composition and structure of the basis metal. Scheil and Würst only found that the presence of some impurities causes a shift in the maximum, but they gave no rules for this shift.

## B. EXPERIMENTAL STUDIES ON THE REACTIONS OF IRON WITH LIQUID ZINC

### § 3. Relationship between the structure of the basis material and the structure of the diffusion layer

The reaction of iron with liquid zinc can produce diffusion layers of different structures and this confirms our earlier assumption that the nature of the phases formed by active diffusion is determined not only by the conditions of equilibrium at the interface but also by other factors.

One of these factors is clearly the state of the surface of the basis metal (iron), which is a "background" for the formation of crystals of a new phase.

Some surface phenomena on metals (adsorption, penetration of gases, galvanic processes) indicate that the structure of the surface has a considerable influence on reactive diffusion.

We started our investigations on the reactions of iron with zinc by clarifying the influence of the basis material of the surface on which the two metals react. We used three types of wire: 1) commercial iron containing 0.1–0.15% C; 2) steel containing 0.45% C; and 3) steel containing 0.9% C. The content of impurities did not exceed Mn—0.3–0.5%; Si—0.15–0.25%; P—0.02–0.04%; S—0.03%.

In our experiments we assumed that only the iron reacted with zinc, and that the amount and distribution of cementite may influence the properties of the basis metal, and thus the conditions of crystallization of new phases.

The specimens were annealed at temperatures  $50^{\circ}\text{C}$  above the  $\text{Ac}_3$  temperature, and then slowly cooled together with the furnace. To prevent appreciable oxidation and the burning of carbon of the surface, the specimens were heated in cast iron turnings.

After they had been annealed, the specimens were etched in a 10% solution of hydrochloric acid, carefully washed, and dried. The zinc used for the experiments was purified by repeated distillation in vacuo. During the reaction the surface of the zinc bath was protected from oxidation by a layer of fused ammonium chloride.

Care was taken to treat the specimens under identical conditions. All the specimens treated at the same temperature were fastened together on a wooden frame, and simultaneously etched and zinc coated under identical conditions. After they had been zinc coated, the specimens were mounted in sulfur, and samples for microscopic examinations were prepared along the plane perpendicular to the zinc-coated surface. The specimens were etched in a 4% solution of picric acid in alcohol. Thus, the structures of the diffusion layer and of the basis material can be seen.

The coating was carried out at 420, 460, and  $500^{\circ}\text{C}$ , and the specimens were held in the molten zinc for 4 minutes.

The microstructures of the diffusion layers obtained under these conditions are shown in Plates 6 and 7 (see Appendix):\*

A study of these microstructures shows that at 420 and  $460^{\circ}\text{C}$  the coatings produced on steel containing 0.15% C (Plate 6) had two layers. The layer closer to the iron was rather thin (about 0.01 mm), and separated by a distinct boundary from the iron and from the second diffusion layer.

The second layer, which was much wider, had crystals clearly oriented perpendicular to the surface of the specimen.

This structure is similar to the one previously obtained by the reaction between electrolytic iron and liquid zinc (Plate 3, Appendix).

Thus, we can assume that the first narrow layer consists of the  $\text{Fe}_5\text{Zn}_{21}$  intermetallic compound (previously called  $\gamma$ -phase), and the second of a  $\text{FeZn}_7$  compound (an  $\epsilon$ -phase according to an earlier nomenclature). These conclusions are based on an X-ray analysis of the coatings, and agree well with the published data, particularly for the  $\text{Fe}_5\text{Zn}_{21}$  compound.

For a more convenient comparison of our results with the published data, we shall henceforth use the nomenclature introduced by Schramm. We shall call the  $\text{Fe}_5\text{Zn}_{21}$  compound a  $\Gamma$ -phase, and the  $\text{FeZn}_7$  compound a  $\delta$ -phase.\*\*

The zinc coating of steel containing 0.15% C at 420 and  $460^{\circ}\text{C}$  produced two diffusion layers, consisting of  $\Gamma$ - and  $\delta$ -phases.

Different results were obtained when steels with 0.5 and 0.9% of C were coated at the same temperatures (Plate 7). The characteristic feature of diffusion layers formed on the surface of these steels is that they contained no narrow, sharply defined layer of the  $\Gamma$ -phase. These coatings consisted of a single  $\delta$ -phase layer, which in structure and orientation

\* Plates 6 and 7 show structures obtained at  $420^{\circ}\text{C}$ . The same structures were obtained at  $460^{\circ}\text{C}$ .

\*\* The  $\Gamma$ -phase is identical with the  $\gamma$ -phase we have already studied, and the  $\delta$ -phase with the  $\epsilon$ -phase. The designations of  $\gamma$  and  $\epsilon$  that we used in Chapter I were correct according to the classification of phases by Hume-Rothery.

resembled the external diffusion layer formed on the surface of iron and steel containing 0.15% C.

The coatings formed on steel with 0.5 and 0.9% C were considerably thicker (particularly on steel with 0.9% C).

The structure of the diffusion layer formed at 500°C was the same on all three types of steel studied, and resembled the structure shown in Plate 7. No  $\Gamma$ -phase was found in coatings obtained at the same temperature on steel with 0.15% C.

A comparison between these results and published data shows that the structures of coatings formed on steel with 0.15% C at 420 and 460°C are very similar to those obtained by the above authors on pure iron at about 500°C (reaction of the second type).

Thus, we found that the differences in the structures of diffusion layers noted by several authors who zinc coated the same materials at different temperatures also exist when different materials are zinc coated at the same temperature.

As we have already mentioned, Tungal, Scheil, and Shtengoff found that the composition of the basis material influences the structure of the coating.

A later paper by Musatti and La Falce /97/ mentions that the solubility of iron decreases with increase in the carbon content. These data contradict our results, and they have not been confirmed by later studies.

Since only the iron reacts directly with zinc, it can be assumed that the changes in the structure of the coating as we pass from pure iron and low-carbon steel to high-carbon steels are due not only to the change in the chemical composition of the steel but also to the change in the structure of the basis metal.

To check the correctness of this assumption, we carried out experiments with steels containing 0.5 and 0.9% C. These steels were heated to 40°C above  $A_{c3}$ , and quenched in ice-cold water. The specimens then had a martensitic structure. They were immersed in liquid zinc at 450°C, and their structure was then studied. It was found that the interaction of these specimens with zinc is similar to the reaction of specimens containing 0.15% C, which means that the coating contained both a  $\Gamma$ -phase and a  $\delta$ -phase (Plate 8, Appendix). These experiments indicate that the differences in the structure of the diffusion layers of zinc on steels of different compositions are due not so much to the different contents of carbon as to the different structures of the basis metal, irrespective of its chemical composition.

#### § 4. Kinetics of the formation and growth of diffusion layers during the reaction of iron with liquid zinc

The kinetics of the process was the main problem in our study of the reaction of iron with liquid zinc.

In earlier research most attention was paid to temperature, and reactions at constant temperature were studied rarely and only at long holding times. Therefore, we investigated not only the influence of temperature, but also the sequence of formation and the growth of the diffusion layers at constant temperature.



To relate this problem to the structure of the basis metal, which as clearly seen in the last section has a certain influence, the experiments were carried out with two types of steel containing 0.15 and 0.9% C.

Research on the kinetics of the process of zinc coating was also useful for determining the conditions under which layers of a maximum mechanical strength can be obtained. These conditions are directly related to the nature of the intermetallic compounds formed during zinc coating, their thickness, and their structure.

As starting material we took steel wire containing 0.15 and 0.9% C (from the same batches and with the same composition as the wire for the experiments described in §3), and commercially pure zinc distilled in vacuo. Since the purpose of our research was to study the dependence of the structure of the coating on the duration and temperature of the process, we used structural methods of analysis, mainly microstructural, which are most important for studying reactive diffusion.

By methods of structural and X-ray analysis, we /70/, like other authors, determined the physicochemical nature of the phases formed during the reaction of iron with zinc. It was usually possible to correctly determine the presence of individual phases from the microstructure of the coatings.\* Therefore, we used X-ray analysis only if the nature of the phases present in the deposit could not be determined from their microstructure alone.

As an additional method for solving certain problems, we used the electrochemical method introduced for studying deposits by Glasunov /98/. Britton /99/ suggested this method for studying zinc coatings on wire, and obtained several types of curves for deposits obtained by different methods (hot-dip coating, electroplating, etc.). In our work this method was adjusted to solve the problems we were studying.

In an electrochemical analysis of zinc deposits, the e.m.f. was measured between zinc-coated specimens (for example, a zinc-coated wire) used as an anode and a zinc gauze which served as a cathode in the dissolution of zinc coatings in a solution of  $\text{ZnSO}_4$ .

If a cell consisting of a zinc-coated wire, pure zinc, and a  $\text{ZnSO}_4$  solution (electrolyte) is short-circuited by an external current, the potential difference  $E$  between the anode and the cathode can be written:

$$E = E_c - E_a + I_r,$$

where  $E_c$  is the potential of the cathode,  $E_a$  is the potential of the anode, and  $I_r$  is the potential drop in the circuit.

Since both  $E_c$  and  $I_r$  are constant for given conditions of the experiment, the potential  $E$  will depend on  $E_a$  only, i.e., on the potential of the anode. By measuring  $E$  during the dissolution of zinc coatings in  $\text{ZnSO}_4$  we can obtain the values of the electrochemical potential  $E_a$  of our deposit at different distances from the surface.

Under the influence of an electric current, a specimen dissolves in an electrolyte in stages. The potential  $E$  remains constant during the dissolution of a layer of constant concentration (pure zinc or an intermetallic compound), and then changes as we pass from one layer to another. Thus,

\* It was sometimes difficult to separate the  $\delta$ -phase from  $\xi$ . This was only possible using data on the regions of existence of these phases in the Fe — Zn phase diagram, or data on their distribution in the structure of the deposits.

the variation in potential with time can be described by a curve like the one in Figure 40.

Sections *BC*, *DE*, and *FG* of the curve correspond to transitional regions of the deposits from pure zinc to the first intermetallic compound, from the first intermetallic compound to the second, etc. Each of these sloping sections of the curve is formed if the coating contains a solid solution (in zinc, in the intermetallic compound, and in iron).

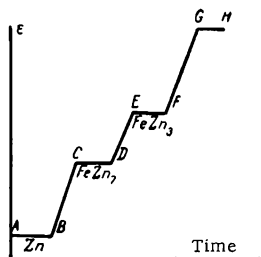


FIGURE 40. Variation in potential with time during the dissolution of zinc-coated iron.

The size of each of the horizontal sections depends on the thickness of the individual layers and on the rate of their dissolution in the electrolyte. This rate clearly varies from layer to layer. Britton believes that the coating is dissolved uniformly from the whole surface of the zinc-coated wire. Even if this is not completely true, it can be assumed that the size of the horizontal plateau is proportional to the thickness of the given part of the deposit.

We used the electrochemical method as a supplement to microstructural analysis for determining the structure of a zinc coating. The shape of the potential-time curve, the number of horizontal sections, their length, and the length of the whole curve, gave us an idea of the intermetallic compounds present in the coating, their relative thickness, and the relative thickness of the deposits obtained under different operating conditions.

The apparatus for recording the curves of the electrochemical potential consisted of a glass vessel 35 mm in diameter, and a cylindrical zinc cathode placed on the internal surface of this vessel.

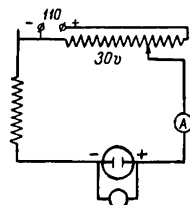


FIGURE 41. The electric circuit diagram.

As an anode we used zinc-coated specimens 65 mm long and 1–1.5 mm in diameter. The cylindrical vessel was covered by an ebonite lid fitted with the terminals of the anode and cathode, separately fastened. The electrolyte was a solution of 20 parts of NaCl and 10 parts of  $\text{ZnSO}_4$  in 100 parts of water. The apparatus was filled with 70 cc of this solution. The current density in the cell was  $0.16 \text{ A/cm}^2$ .

A diagram of the electric circuit is given in Figure 41.

After the specimen had been immersed in the solution and the current switched on, we measured the potential difference between the anode and cathode, usually every 20 sec. The measurements were stopped after all the zinc coating had dissolved in the solution. The end of the process was found from the potential difference, which in this case corresponded to that between an iron anode and zinc cathode.

The mechanical strength of the deposits was determined by the usual simple methods used in plants. These include tests on the cracking and peeling of the zinc layer as a result of the deformation of a zinc-coated wire.

The zinc-coated wire was wound around a rod 4 mm in diameter. We did not use the different industrial standards, as we only wished to study

the influence of the conditions of zinc coating on the strength of the deposit. Therefore, it was important to maintain the same conditions of testing.

Such tests correspond to the service conditions of the wire.

a) Formation and growth of diffusion layers at 450°C. To study the isothermal formation of zinc deposits we chose 450°C as the temperature most frequently used in industry for zinc coating iron and steel.

Iron (0.15% C) and steel (0.9% C) specimens made of 1–1.5 mm thick wire were treated by the above procedure.

The specimens were held for a given time in the zinc bath, and then rapidly withdrawn and wiped with asbestos. The process is thus similar to the industrial method, in which wiping with asbestos is a necessary operation in the zinc coating of wire to impart a smooth and uniform surface. We had to do this to gain a correct idea on the mechanical strength of the deposit. A smooth and uniform surface is advantageous for the electrochemical analysis of the deposits.

To obtain a better idea on the microstructure of the coating, we carried out another series of experiments with the same starting material but without wiping. In these experiments the specimens were held for a given time in the melt, and then rapidly cooled together with the liquid zinc, which usually solidified in the course of a few seconds.

The microstructures of zinc deposits on iron specimens (0.15% C) cooled together with the melt are shown in Plates 9 and 10 (see Appendix). Layers obtained by immersing for less than 1 min had the structure of a fine-grained eutectic ( $\text{FeZn}_7 + \text{Zn}$ ) ingrained with small crystals, apparently of  $\text{FeZn}_7$  ( $\delta$ -phase). No layer of an  $\text{Fe}_5\text{Zn}_{21}$  compound was found.

Quite different structures are obtained by immersing for 1 min. These coatings have a clearly defined layer of the  $\text{Fe}_5\text{Zn}_{21}$  compound bordering on the iron basis. The structure of the external layer bordering on zinc is also different. Instead of the disordered distribution of the  $\text{FeZn}_7$  crystals in the eutectic, characteristic of short holding times, we have no eutectic but a clearly defined orientation of crystals perpendicular to the surface of the basis metal.

The structure of the layers obtained by longer immersion did not differ. The formation of a visible and continuous layer of the  $\text{Fe}_5\text{Zn}_{21}$  compound inhibits further growth of the whole coating, particularly of the  $\text{FeZn}_7$  layer. Plates 9 and 10 (in the Appendix) show that an increase in the holding time from 3 to 20 min scarcely changes the thickness of the  $\text{FeZn}_7$  layer. The layer of  $\text{Fe}_5\text{Zn}_{21}$  increases continuously. The law governing the growth of this phase was determined by measuring the thickness of the layer formed by immersing for different times (from 1 to 20 min).

Mean values of the thickness of the  $\text{Fe}_5\text{Zn}_{21}$  layer are given in Table 42.

TABLE 42.

Duration of zinc coating, min	Thickness of layer, $y \times 250 \text{ mm}$	$y^3 \times (250)^2 \text{ mm}^2$
1	1	1
3	2.5	6.2
5	4.5	20.2
7	4.5	20.2
10	6	36
20	8.5	72.2

The graph of the square of the thickness of this layer plotted against time (Figure 42) is a straight line on which the experimental data lie satisfactorily. Hence it follows that the growth of the chief phase ( $\text{Fe}_5\text{Zn}_{21}$ ) is governed by a parabolic law expressed by the formula  $y^2 = 2pt$ , where  $p$  is a constant proportional to the diffusion coefficient at a given temperature.

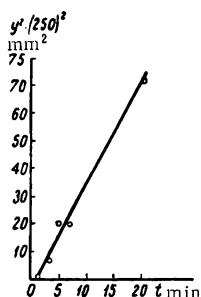


FIGURE 42. Curve showing the growth of the chief  $\Gamma$ -phase.

This result is quite clear, since the  $\Gamma$ -phase satisfies the limiting conditions necessary for parabolic growth of the diffusion layer. In fact, as we have already mentioned, the condition for parabolic growth includes the constancy of the concentration on the boundary of the layer. The  $\Gamma$ -phase borders on the intermetallic compound  $\text{FeZn}_7$ , which has a slightly variable composition, and also on  $\alpha$ -iron, which has a concentration that can be considered constant, since the diffusion of zinc in  $\alpha$ -Fe at  $450^\circ\text{C}$  is so slow that it can be neglected. Deviations in the growth of the  $\Gamma$ -phase from the parabolic law can be observed for longer immersions in the zinc bath only.

The layer of the  $\delta$ -phase is not governed by the formula  $y^2 = 2pt$ , and after the  $\text{Fe}_5\text{Zn}_{21}$  compound has been formed, the growth of the  $\delta$ -phase is greatly retarded.

The microstructural study of the coatings was supplemented by the electrochemical method described above. We obtained a series of curves in potential-time coordinates for specimens coated with zinc at  $450^\circ\text{C}$  for different immersion times. These curves (Figure 43) indicate that if the zinc coating process is short (up to 45 sec), the horizontal plateaus corresponding to phases with a constant composition (in this case intermetallic compounds) are missing. The first, small plateau, or more accurately bending point, appears after 45 sec of immersion in the zinc bath, and it can be seen quite clearly in the case of specimens coated for more than 1 min. Processes lasting for more than two minutes produce a second plateau on the curve which corresponds to a higher potential.

The lower plateau is more pronounced and longer, and apparently corresponds to the  $\delta$ -phase ( $\text{FeZn}_7$ ), and the upper plateau represents the higher potential, and corresponds to the chief  $\Gamma$ -phase. The small thickness of the chief phase explains its relatively small effect on the electrochemical curves. None of the curves has a horizontal plateau corresponding to pure zinc, which is understandable because all specimens were wiped with asbestos directly after they were removed from the zinc bath, and therefore a layer of liquid zinc was removed from the surface of the wire.

The electrochemical curve confirmed the data of the microstructural analysis.

Zinc-coated wire was tested by winding it around a 4 mm-diam. rod. It was shown that specimens treated at  $450^\circ\text{C}$  for 45 sec—1 min are of good quality, and no defects appear during the test. Coatings obtained by processes lasting for one min or more crack and peel during this test. A comparison of these results with those of the microstructural analysis shows that after the intermetallic  $\text{Fe}_5\text{Zn}_{21}$  layer is formed, the adhesion of zinc coatings greatly deteriorates. This is apparently due to the weak bond between this intermetallic compound and the iron basis.

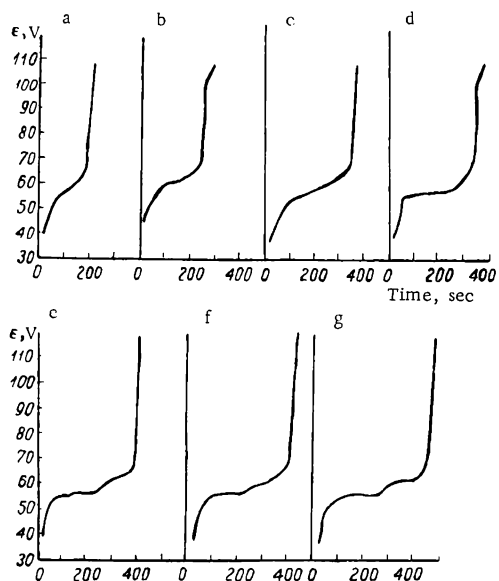


FIGURE 43. Electrochemical curves of zinc coatings on iron (0.15% C):

Duration of zinc coating: a—15 sec; b—30 sec; c—45 sec; d—1 min; e—2 min; f—3 min; g—5 min.

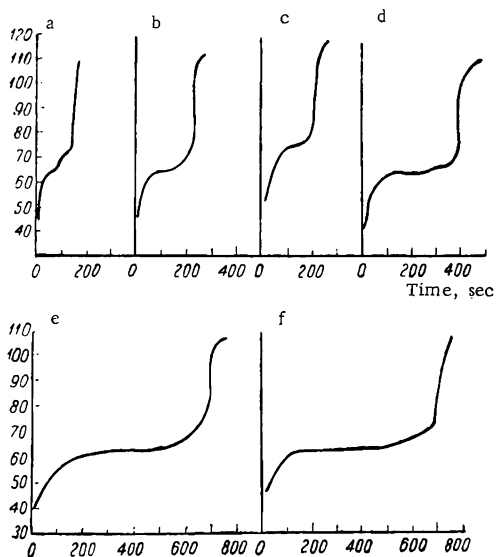


FIGURE 44. Electrochemical curves of zinc coatings on steel (0.9% C):

Duration of zinc coating: a—15 sec; b—30 sec; c—42 sec; d—1 min; e—2 min; f—3 min.

A certain influence may be exerted by the change in the structure of  $\text{FeZn}_7$  crystals, caused by the formation of the  $\text{Fe}_5\text{Zn}_{21}$  compound. An orientation of the  $\text{FeZn}_7$  crystals probably decreases the strength of the layer.

Electrochemical curves for zinc-coated steel wire are shown in Figure 44. These curves have only a single plateau, which apparently corresponds to the intermetallic  $\text{FeZn}_7$  compound.

The electrochemical curves constructed for iron and steel wire show the rate of growth of the diffusion layer during the zinc coating of iron and steel at  $450^\circ\text{C}$ .

If we neglect the difference between the rates of dissolution of diffusion intermetallic iron-zinc compounds in  $\text{ZnSO}_4$ , and consider the time necessary for dissolution of the total zinc coating (width of the electrochemical curve) in relation to the thickness of the coating, we can find the relationship between the thickness of the deposit and the duration of zinc coating.

Such curves plotted in the coordinates: duration of zinc coating — thickness of coating (time of dissolution of coating in  $\text{ZnSO}_4$  under current) are shown in Figure 45 for iron and steel wire.

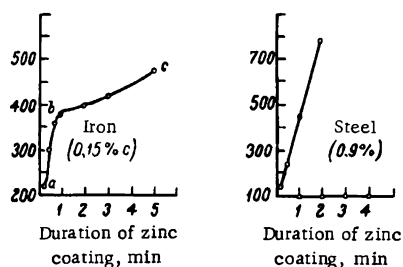


FIGURE 45. Duration of the dissolution of layers in  $\text{ZnSO}_4$ , in sec.

These curves confirm our conclusions derived from the results of microstructural analysis. For iron wire the thickness of the deposits grows rapidly up to a certain limit of duration (1 min) of the zinc coating process. Further increase in the duration of coating leads to a much slower growth of the layer. According to microstructural analysis, the bending point on the growth curve clearly indicates the formation of an  $\text{Fe}_5\text{Zn}_{21}$  intermetallic compound. For steel wire (Figure 44) the graph showing the continuous growth of the layer is a straight line.

The differences in the kinetics of growth of diffusion layers on iron and steel are indicated by the action of liquid zinc on the baths used for coating. It has been experimentally confirmed (for example, at the Lus'vensk Metallurgical Works) that with decrease in the content of carbor in the material of which the bath is made, the reaction with liquid zinc becomes less vigorous, and consequently the service life of the device is prolonged. This phenomenon is partially explained by the results of our research, which indicate that with decrease in the carbon content in the iron the  $\text{Fe}_5\text{Zn}_{21}$  compound is formed more rapidly, and its presence greatly hinders the reaction between iron and liquid zinc.

b) Influence of temperature on the kinetics of growth of diffusion layers. Numerous studies have been carried out on the influence of temperature on the structure of zinc coatings. The most important of these have already been discussed. We have seen that the most significant result of these studies was the discovery of two types of reactions to explain the maxima on the curves showing the temperature dependence of the rate of dissolution, or of the rate of growth, of diffusion layers of iron.

These conclusions were drawn for pure iron and for prolonged durations of coating in liquid zinc.

The purpose of the present research was to determine the nature of the reaction at the initial stage of the process, and therefore unlike previous authors we held the specimens in liquid zinc for very short periods.

For the basis material we used: pure iron containing less than 0.1% C, steel containing 0.15% C, and steel containing 0.9% C.

The structure of deposits on pure iron was studied after zinc coating at 450, 475, 500, 525, and 550°C. The conclusion drawn from this study is that zinc coating at 450°C produces the same results as those we obtained with steel containing 0.15% C, except that here, too, when the content of carbon in the specimens was lower, the  $\Gamma$ -layer appeared early (after coating for 30 sec). The same is true of zinc coating at 475°C, when the  $\Gamma$ -layer appears even after a 15-sec dip. A comparison of the structures obtained after 15 sec and 2 min in the bath at 475°C showed that the total thickness of the layer scarcely increased, except for the  $\Gamma$ -phase which became thicker as the result of the growth of  $\text{FeZn}_7$  crystals.

No  $\text{Fe}_5\text{Zn}_{21}$  compound was found after zinc coating at 500°C. The deposit consisted of only one layer, a eutectic with coarse and light ingrained crystals. According to Scheil and Würst /93/, this is a  $\delta$ -phase.

Zinc coating at 525 and 550°C for periods from 15 sec to 2 min produces only a  $\Gamma$ -phase layer.

The results of the microstructural analysis show that the diffusion layer grows most rapidly at 500°C. At 525 and 550°C a process lasting from 15 sec to 2 min produced coatings of almost the same thickness.

An X-ray analysis of the structure of deposits, already described, showed that  $\text{Fe}_5\text{Zn}_{21}$  and  $\text{FeZn}_7$  compounds are formed at 450 and 475°C. Only  $\text{FeZn}_7$  is formed at 500°C and only  $\text{Fe}_5\text{Zn}_{21}$  at 525 and 550°C. Thus, these results confirmed the data of microstructural analysis.

Structures of the same type were formed by zinc coating steel containing 0.15% C, but they varied in a somewhat different manner. A microstructural analysis showed that coatings obtained at 475 and 550°C consist of two layers of the same structure as the coatings formed at 450°C. Coatings obtained at 500 and 525°C contain no  $\text{Fe}_5\text{Zn}_{21}$  compounds, but only a single diffusion layer with the same structure as that produced on pure iron at 500°C. The thickness of this layer, as on pure iron, is considerably greater than the total thickness of the diffusion layers formed below 500 and above 525°C.

Thus, deposits obtained on pure iron ( $< 0.1\%$  C) have a single-layer structure formed between 500 and 525°C, while deposits obtained on steel containing 0.15% C have such a structure formed between 500 and 550°C.

From a study of structures formed at different temperatures on steel containing 0.15% C it was possible to verify our conclusions on the nature of diffusion phases.

A comparison of deposits obtained at 450, 475, and 500°C shows that they have the same structures, and therefore there can be no doubt that the phases formed at these temperatures are identical. On the other hand, the most recent Fe—Zn phase diagram, and particularly the extensive studies of Schramm, indicate that above 530°C the coating consists of  $\Gamma$ - and  $\delta$ -phases only. Consequently, the coatings on pure iron and on low carbon steel obtained at all the above temperatures consist of  $\Gamma$ - and  $\delta$ -phases.

We studied the structure of coatings on steel containing 0.9% C at 475, 500, and 525°C obtained by immersions lasting 10 and 20 sec. In all cases the structure was the same as that obtained on iron and steel containing 0.15% C at 500°C, and consisted of elongated thread-like crystals of FeZn<sub>7</sub>, which were transformed into a fine-grained eutectic mixture (FeZn<sub>7</sub>+Zn).

c) Discussion of results. Kinetics of the reaction of iron with liquid zinc. Our data on the influence of temperature agree in general with those of other authors, including the most convincing data of Scheil and Würst. These data disagree on the structure of zinc coatings formed on pure iron at 450°C. Scheil and Würst maintain that these coatings consist of  $\Gamma$ -,  $\delta$ - and  $\xi$ -phases, but we found only the first two of these. The identity of the structures of deposits obtained at 450 and 550°C proves that no  $\xi$ -phase is formed at 450°C. This discrepancy can be explained by the fact that our immersion times (up to 70 min) were considerably shorter than those of Scheil and Würst, and that this time was insufficient for the formation of the  $\xi$ -phase. There were no discrepancies with reference to structures formed above 450°C. Some authors believe that the  $\xi$ -phase is formed below 490—500°C, although it exists up to 530°C. Moreover, Grubitsch /92/, Scheil and Würst /93/, and others agree that this phase has little influence on the kinetics of the reaction of iron with zinc, which is determined chiefly by the relationship between the  $\Gamma$ - and  $\delta$ -phases, and therefore we shall henceforth consider that only these phases are formed. This is in any case true when the immersion times do not exceed 20 min.

By investigating the structure of coatings obtained by short-time immersions in liquid zinc, we were able to clarify details of the process, such as the order of formation of diffusion phases, that had not yet been studied.

It was found that below 500°C separate, sharply defined layers of  $\Gamma$ - and  $\delta$ -phases are almost simultaneously formed during short-time immersions in liquid zinc.

Above 500—525°C, depending on the composition, the  $\Gamma$ -phase is formed first. This is confirmed by the fact that coatings obtained by immersion for up to 3 min consist of a  $\Gamma$ -phase only.

In this research we are the first to show the influence of the structure of the basis metal on the structure of the diffusion layer.

We shall analyze the structures obtained at different temperatures and immersion times by first discussing the results of zinc coating pure iron (C<0.1%) and low-carbon steel (0.15% C). These results indicate the formation of the following two coatings: a two-layer coating ( $\Gamma$ - and  $\delta$ -phases) formed above and below the range of 500—525°C, and a single-layer coating (FeZn<sub>7</sub>+eutectic) formed at 500—525°C.

Some authors found that each of these coatings produces a different curve showing the solubility of iron in liquid zinc as a function of time.



They therefore assumed that there are two types of reactions. We believe that we can explain the variation in the structure of deposits with temperature without such an assumption.

If we disregard the structure formed at 500°C, and thus the maximum on the solubility curve, we can come to the following conclusions on the basis of microstructural analysis: the  $\Gamma$ -layers form at a certain period after the start of the reaction. This period decreases with temperature. Thus, at 450°C the  $\Gamma$ -layer is formed after 30–45 sec, at 475°C it appears after 15 sec, and at 550°C even sooner, since after 15 sec it has an appreciable thickness. There is a certain initial period during which the  $\Gamma$ -layer forms very slowly or not at all.

The  $\Gamma$ -layer grows partially at the expense of the  $\text{FeZn}_7$  crystals and the growth is governed by a parabolic law. The total thickness of the coating increases very slowly. This explains the structure formed by zinc coating pure iron at 525 and 550°C. Here, the  $\Gamma$ -layer appears during the first moment after the specimens are immersed in the bath. Direct contact between iron and liquid zinc is broken, and the dissolution which can proceed only as a result of the diffusion of iron atoms through the continuous  $\Gamma$ -layer is partially slowed down. This also slows down the formation of  $\text{FeZn}_7$  crystals, and therefore short-time immersions produce only  $\Gamma$ -layers. Since iron nevertheless dissolves in zinc, although slowly, longer holding times produce  $\delta$ -layers also.

This order is upset at 500°C, as paradoxically this temperature causes a more intensive dissolution of iron and the formation of different diffusion layers than in the case of zinc coating at other temperatures. These phenomena are the result of a different process, and other conditions being equal, this process is characteristic at temperatures near 500°C. We found no reasons for such a change in the process over this narrow range of temperatures, since neither zinc nor iron undergo any changes in this region. The Fe–Zn phase diagram does not indicate any specific changes at these temperatures.

Therefore an attempt was made to explain the reactions at 500°C within the same framework as the reactions at other temperatures.

Certainly, this framework must be based on the rates of the processes taking place during the reaction of iron with liquid zinc.

There are two main processes during the reaction of iron with liquid zinc: 1) dissolution of iron in zinc, and 2) formation of intermetallic compounds.

The first process is based on the passage of Fe ions into the liquid zinc, and the formation of a solution of a certain concentration. If the concentration of this solution is below the solubility of iron in zinc at the given temperature (short-time process), no solid phases are formed during the process, and only the  $(\text{FeZn}_7 + \text{Zn})$  eutectic, or a eutectic with an excess of  $\text{FeZn}_7$  crystals uniformly distributed in its bulk, crystallizes after the specimens are extracted from the melt. If the concentration of iron in the liquid zinc is higher than its solubility (long-time process),  $\text{FeZn}_7$  crystals will form and will solidify on the surface of the iron specimen. However, some crystals may become detached from the surface of the specimen and enter the melt. After the iron specimen has been extracted from the bath, coarse  $\text{FeZn}_7$  crystals and a eutectic with uniformly distributed  $\text{FeZn}_7$  crystals will probably solidify on its surface.

It can be assumed that the rate of growth of the  $\text{FeZn}_7$  diffusion layer is proportional to the rate of dissolution, provided that the dissolution of iron in liquid zinc is the only process taking place during the coating. As the rate of dissolution we understand the value of  $dQ/dt$  (amount of dissolved substance per unit time) related at each temperature to the moment the reaction starts.

In the second process the  $\text{Fe}_5\text{Zn}_{21}$  compound is formed, and the process can proceed simultaneously with the first, but it is not related to it directly, as this is not a diffusion but a reactive process. We found by experiment that the formation of the  $\text{Fe}_5\text{Zn}_{21}$  layer does not start at the beginning of the process, but a layer which can be observed under a microscope appears a certain time after the reaction starts. We were unable to find out whether this layer is not formed at all during the initial period, or whether it grows very slowly. The period between the start of the process and the moment a layer becomes visible under a microscope can be called the "incubation period"  $t$ , and  $1/t$  the rate of formation of the  $\text{Fe}_5\text{Zn}_{21}$  compound. We have thus found two values characteristic of the interaction of iron with zinc:  $dQ/dt$  is the rate of dissolution; and  $1/t$  is the rate of formation of the  $\Gamma$ -phase. As we know nothing about the temperature dependence of these values, we can only assume that it will be monotonous, and that the curves representing these dependences will have no minimum or maximum. It can also be assumed in general that the temperature dependence of the rate of dissolution will be exponential in nature.

We related the rate of dissolution of iron in zinc ( $dQ/dt$ ) to the start of the process, so that this value could be considered as independent and characteristic of the given process. Otherwise, the rate of dissolution would be influenced by the presence of the  $\text{Fe}_5\text{Zn}_{21}$  compound formed sometime after the coating process has started, and which greatly decreases the final rate of dissolution.

The structure of Zn coatings is determined by the relationship between the above rates and the given conditions. This relationship is in turn influenced by a number of factors, including the temperature of the coating process and the structure of the basis metal.\* We shall now prove that the formation of zinc coatings of various structures at different temperatures can be explained by the above theories. For this purpose, it is necessary to plot the rates of these processes against temperature, and determine which of these can represent the real structure.

We shall not consider the shape of these curves in detail, but they must be monotonous for the following reasons: if the rate of dissolution of iron in zinc is equal to, or slightly more rapid than, the rate of formation of  $\text{Fe}_5\text{Zn}_{21}$ , the immersion of iron specimens into liquid zinc should lead to dissolution of iron in zinc during the first moment of contact, with the formation of a eutectic and  $\text{FeZn}_7$  crystals. Soon after, the  $\text{Fe}_5\text{Zn}_{21}$  compound is formed, which greatly hinders further dissolution of iron. The same is true of zinc coating at 450 and 475°C.

The rate of dissolution of iron in zinc considerably exceeds the rate of formation of the  $\text{Fe}_5\text{Zn}_{21}$  layer, since the iron on the surface of the specimen in contact with the liquid zinc rapidly passes into the solution, and the reaction of formation of  $\text{Fe}_5\text{Zn}_{21}$  on the surface is slowed down or may not proceed at all. This agrees with our observations during zinc coating at 500°C (or at 525°C on steel containing 0.2% C).

\* And also impurities in the bath, as we shall show later.

Finally, if the rate of formation of  $\text{Fe}_5\text{Zn}_{21}$  is more rapid than the dissolution of iron in zinc, the  $\text{Fe}_5\text{Zn}_{21}$  formed during the first moments of the reaction hinders further dissolution of iron, and the  $\text{FeZn}_7$  compound is not formed during the first moments. The same is true at  $550^\circ\text{C}$ .

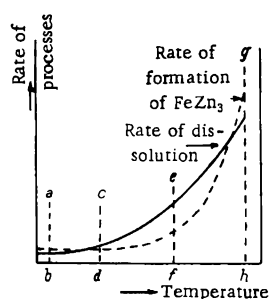


FIGURE 46. Kinetic scheme of the reaction of iron with zinc.

It can be assumed that the rate of dissolution of iron in pure zinc before the  $\text{Fe}_5\text{Zn}_{21}$  compound is formed increases with increase in temperature according to an exponential law. The temperature dependence of the formation of the  $\text{Fe}_5\text{Zn}_{21}$  compound (that is a value inversely proportional to the time after which this layer is formed) is not known, and it can only be assumed that other conditions being equal (for example, the structure of the basis material) the curve representing this dependence will be continuous and monotonous. Figure 46 shows schematically the arrangement of these curves.

This arrangement of the curves of the rate of dissolution of iron in zinc (growth of  $\text{FeZn}_7$ ) related at each temperature to the start of the process and to the rate of formation of  $\text{Fe}_5\text{Zn}_{21}$  can explain the structures of the zinc deposits formed at the corresponding temperatures.

At temperatures corresponding to the sections  $ab$  and  $cd$  ( $450$  and  $475^\circ\text{C}$ ), the rate of dissolution and the rate of formation of  $\text{Fe}_5\text{Zn}_{21}$  are very close, and therefore the beginning of dissolution is followed by the formation of a  $\text{Fe}_5\text{Zn}_{21}$  layer. The formation of this layer inhibits the dissolution of iron. As a result, the structure of the deposit will consist of two layers of  $\text{Fe}_5\text{Zn}_{21}$  and  $\text{FeZn}_7$  compounds, and an increase in the duration of zinc coating will lead to growth of the  $\text{Fe}_5\text{Zn}_{21}$  layer at the expense of the  $\text{FeZn}_7$  layer.

At a temperature corresponding to the section  $ef$  ( $500^\circ\text{C}$ ), the rate of dissolution of iron is much more rapid than the rate of formation of  $\text{Fe}_5\text{Zn}_{21}$ , and therefore at this temperature  $\text{FeZn}_7$  crystals are mainly produced.

Finally, at temperatures corresponding to the section  $gh$  and above ( $525 - 550^\circ\text{C}$ ), the rate of formation of the  $\text{Fe}_5\text{Zn}_{21}$  layer is more rapid than the rate of dissolution of iron, and therefore this compound is formed during the first moments of zinc coating, and hinders the dissolution of iron in zinc from the beginning. In this case the coating can consist of either  $\text{Fe}_5\text{Zn}_{21}$  crystals only (as in the case of coatings obtained by short-time immersions), or of a layer of  $\text{Fe}_5\text{Zn}_{21}$  and a layer of  $\text{FeZn}_7$ .

The curves shown in Figure 46 should be considered as an attempt to explain the structure of zinc deposits by a variation in the ratios between the rate of dissolution of iron in zinc and the rate of formation of a new phase, at different temperatures and at a continuous and monotonic courses of each of these processes.

In this way it is also possible to explain the structures formed during the zinc coating of steel containing  $0.9\%$  C. As we have already seen, no  $\Gamma$ -phase ( $\text{Fe}_5\text{Zn}_{21}$ ) is formed over the range of  $450 - 550^\circ\text{C}$ .

It is sufficient to assume that the influence of the structure of the basis material can lead to a change in the relationship between the rate of formation of the  $\Gamma$ -phase ( $\text{Fe}_5\text{Zn}_{21}$ ) and the rate of dissolution of iron in liquid zinc.

On eutectoid steel (0.9% C), the rate of dissolution at all temperatures is apparently much more rapid than the rate of formation of the  $\Gamma$ -phase. As a result, only a single-layer structure of  $\text{FeZn}_7$  crystals is formed, and in the layers removed from the surface this is gradually transformed into a ( $\text{FeZn}_7 + \text{Zn}$ ) eutectoid. This structure is similar to that obtained on pure iron or on low-carbon steel over a narrow temperature range near  $500^\circ\text{C}$ .

It should only be pointed out that as already shown (§3) this influence is due to changes accompanying the change in the chemical composition, and not directly to the influence of the carbon content in the iron.

Let us once again mention the strength of zinc coating. This problem cannot yet be discussed in detail since so far we have only considered the processes occurring during zinc coating of iron and steel in pure zinc.

In some plants which galvanize iron and steel, special additions (chiefly aluminum) are introduced to increase the strength of the coating. Therefore, a complete review of the problem of the strength of zinc coatings must be based on an analysis of the influence of some impurities on the structure of the coating.

Nevertheless, some products (wire, tubing, various metallic articles) are zinc coated in baths with no special additions. Therefore, the problem of the conditions for producing strong layers without additions to the bath is of industrial interest.

It has been found that zinc coatings adhere most strongly to the basis material if there are no intermediate intermetallic phases between them. However, to produce such coatings with a sufficient thickness by hot dipping in pure zinc is almost impossible. Therefore, we must search for a better solution to the problem when intermediate alloy layers are present.

The results of this research have shown that the  $\text{Fe}_5\text{Zn}_{21}$  intermetallic compound adheres badly to the basis material, and therefore it is least favorable for zinc coatings.

The rate of formation of this phase is greatly influenced by the structure of the basis material and by the temperature of the process.

Zinc coating of pure iron at  $450^\circ\text{C}$  in baths with no special additions leads to the formation of an  $\text{Fe}_5\text{Zn}_{21}$  layer a short time after the reaction starts. This time decreases if the content of carbon in the iron is less.

Deposits obtained by short-time immersion of iron and steel (before  $\text{Fe}_5\text{Zn}_{21}$  layers can be formed) consist of an ( $\text{FeZn}_7 + \text{Zn}$ ) eutectic with very small  $\text{FeZn}_7$  crystals ingrained in the total mass of the coating.

The absence of any coarse intermetallic precipitate and of any intermediate boundaries indicates that for zinc coating with pure zinc the structure of a fine-grained eutectic is the most favorable for strong deposits.

The correctness of this assumption was confirmed by using two examples of such a structure obtained by: 1) a short-time zinc coating of iron (up to 45–60 sec) at  $450^\circ\text{C}$ ; and 2) a longer immersion (up to 2–3 min) at  $500^\circ\text{C}$ .

Therefore, we can ask whether thick deposits cannot be obtained at  $500^\circ\text{C}$ , when no  $\text{Fe}_5\text{Zn}_{21}$  intermetallic compound is formed during rather

long periods of immersion. However, zinc coating at 500°C involves some difficulties, because in order to obtain a coating without an  $\text{Fe}_5\text{Zn}_{21}$  layer the temperature must be controlled very accurately. This is difficult under industrial conditions.

Zinc coating at elevated temperatures (about 500°C) when no  $\text{Fe}_5\text{Zn}_{21}$  layer is formed must be applied to definite technical articles.

These articles may be iron wire, which is often zinc galvanized. Usually, to obtain a smooth surface the coated wire is wiped, and a layer of liquid zinc removed. If it were technically and economically feasible to increase the temperature of the bath for wire coating to 500°C, it would not be necessary to wipe the wire (or at least the wire could be wiped less), since because of the increased liquidity of zinc the surface of the coated wire would remain sufficiently smooth without wiping, or would require only slight wiping.

The production of zinc deposits with a satisfactory surface finish and appreciable thickness would also favorably influence the corrosion resistance of zinc-coated wire, since it has been found that the surface layer which consists of pure zinc is the most corrosion resistant, and that this resistance is greatly reduced by removing the surface layer.

Usually, the rate of zinc coating of iron wire is so great (the average rate of passage of wire is 30–60 m/min in a 9-m long bath) that the  $\text{Fe}_5\text{Zn}_{21}$  layers are not sufficiently thick to have much influence on the strength of the coating, and therefore if the process of zinc coating is correctly chosen, especially with reference to rate and temperature, and if the wire is correctly treated before the coating process, it is possible to obtain sufficiently strong deposits at 450°C also, provided that the deposits produced are not too thick.

On annealed steel wire no  $\text{Fe}_5\text{Zn}_{21}$  layer can be formed at all, and a decrease in the strength of the coating may be due to the intense growth of acicular  $\text{FeZn}_7$  crystals during long-time processes only.

We must remember that very often the steel wire enters the zinc bath after heat treatment involving rapid cooling rates.

We have found that the structure of deposits is greatly influenced by the preliminary heat treatment, and that rapid cooling of steel from above the  $\text{Ac}_3$  point can lead to the formation of an  $\text{Fe}_5\text{Zn}_{21}$  phase even during short-time zinc-coating processes. Therefore, on zinc-coated steel wire we can often find deposits with a structure similar to that formed on iron.

The strength of zinc deposits is particularly important for galvanized sheet, since the coatings on this are usually thicker than on wire. It has been experimentally found that no deposits with a satisfactory strength can be formed on sheets obtained from a bath containing only commercially pure zinc. Special additions are therefore introduced, chiefly aluminum.

The structure and the strength of zinc deposits from baths containing aluminum will be discussed below.

## **§5. Influence of aluminum in zinc baths on the structure and strength of zinc coatings**

It was not the purpose of our research to study the influence of a third component on the processes of reactive diffusion between two metals,

since this problem has recently been widely investigated by Oknov and Gluskin /100/, and also by Gluskin /101/. We shall discuss this problem mainly in connection with the practical task of obtaining strong zinc deposits, which we shall describe in the next section. We wished to clarify the kinetics of the process of zinc coating discussed in the last section. We also studied the influence of aluminum on zinc coating.

The favorable influence of aluminum on the quality of zinc coatings is well known. Nevertheless, the nature of this influence, and its dependence on the structure of the deposits, are questions which have not yet been solved.

As starting material for our research we used sheets of commercial iron containing about 0.1% C, and commercial zinc distilled in vacuo. Electrolytic zinc was used for control tests and aluminum 99.5% pure. The specimens were 1 cm wide and 10–15 cm long and were cut from the same iron sheet. To study coatings by the electrochemical method we used an iron wire containing 0.1% C.

Before the specimens were coated, they were pickled for 20 minutes in a 10% solution of sulphuric acid at 65°C, washed in running water, and then covered with a saturated solution of zinc chloride.

The coatings were studied by microstructural and electrochemical methods. The strength was tested by bending the specimens through 180° using a wooden hammer (as in the tests carried out in plants).

First, we studied the structures of deposits formed at 450°C, the temperature usually used in industry.

The addition of up to 0.1% of aluminum to the bath produced no visible changes in the structure of the coating, which like the coatings obtained from baths of pure zinc consisted of two layers,  $\text{Fe}_5\text{Zn}_{21}$  and  $\text{FeZn}_7$ . Baths containing 0.1% Al produced single-layer coatings ( $\Gamma$ -phase).

The  $\text{Fe}_5\text{Zn}_{21}$  layers produced by short-time immersions (20 sec) in baths containing 0.1% Al did not cover the whole surface of the article but formed separate patches.

Coatings obtained from baths with 0.2% Al consist of pure zinc with no  $\text{Fe}_5\text{Zn}_{21}$  or  $\text{FeZn}_7$ .

The  $\text{Fe}_5\text{Zn}_{21}$  compound is sometimes formed in baths containing 0.2% Al, but only as separate patches covering small areas. No intermetallic phases are formed in baths containing from 0.2% to 5% Al.

The above results indicate that as the content of aluminum in the zinc bath is increased, there is some inhibition of the processes of formation of iron–zinc alloys, that is of the chemical reaction on the surface leading to the formation of  $\text{Fe}_5\text{Zn}_{21}$ , and of the solubility of iron in liquid zinc with the formation of  $\text{FeZn}_7$  crystals and a eutectic. It can be assumed that aluminum influences the solubility of iron in zinc more than the reaction of formation of  $\text{Fe}_5\text{Zn}_{21}$ .

A study of the mechanical strength of deposits showed the following:

The bending tests on specimens coated in baths of pure zinc always lead to peeling of the coating. The same results were obtained with deposits coated in baths containing 0.05% Al. Baths containing from 0.1 to 0.2% Al produced coatings with better adhesion; peeling was not observed from the whole edge of the bent specimens but only from part. Coatings from baths with 0.2% Al peeled off only rarely, and then only from small areas. Finally, baths with more than 0.2% Al gave coatings which did not peel.

A comparison of these results with the data of microstructural analysis showed that the strongest coatings are those with no intermetallic layers. Such coatings can be produced in a bath containing a certain amount of aluminum. We found that for immersions of up to 1 min at 450°C the bath must contain at least 0.2% Al.

Coatings from baths with a lower content of aluminum probably contain intermetallic layers, particularly  $\text{Fe}_5\text{Zn}_{21}$ . This will lead to peeling of the coating during the formation of sheet. Coatings from baths containing at least 0.7% Al have an Al—Zn eutectic layer bordering on the iron. The amount of this eutectic increases gradually with increase in the content of aluminum in the bath, and covers the whole surface of the article when the bath has 5% Al. These data agree with the Al—Zn phase diagram, which indicates the start of formation of a eutectic at 1% Al. Thus, iron has no influence on the interaction between zinc and aluminum in hot-dip zinc coating baths, since aluminum greatly decreases the solubility of iron, which passes into the bath in such small amounts that it cannot influence the structure of Al—Zn alloys.

The data of microstructural analysis were supplemented by electrochemical curves of the deposits on iron (0.1 % C) wire formed by the above method at 450°C from baths with different contents of aluminum.

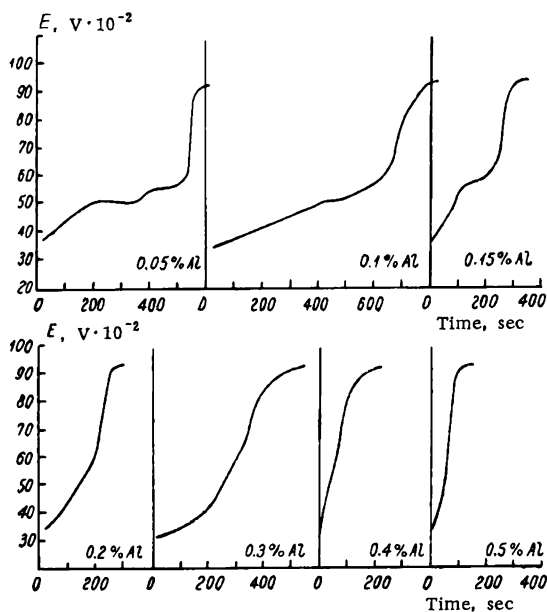


FIGURE 47. Electrochemical curves of zinc coatings obtained from baths with different aluminum contents.

These curves are given in Figure 47. The curves for 0.05% Al have two plateaus, apparently corresponding to  $\text{Fe}_5\text{Zn}_{21}$  and  $\text{FeZn}_7$ . The curves for 0.1 % Al have two plateaus, but the upper one is much shorter. The

curve for 0.15% Al has only one plateau corresponding to  $\text{Fe}_5\text{Zn}_{21}$ . No plateaus were found on the electrochemical curves obtained from baths

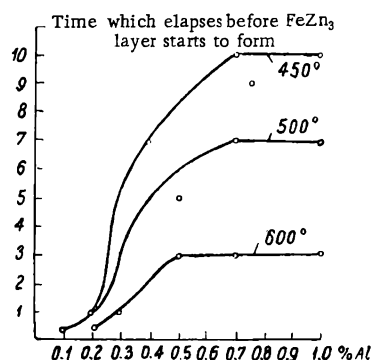


FIGURE 48. Influence of aluminum on the formation of  $\text{FeZn}_3$ .

with 0.2% or more Al. Thus, the data of electrochemical analysis agree with those of microstructural analysis.

In this connection it was interesting to find whether the intermetallic compounds disappear altogether if the baths contain >0.2% Al, or if their formation is hindered at elevated temperatures or by long-time immersion. This would indicate that aluminum does not stop the reaction between iron and liquid zinc but only hinders the dissolution of iron and the formation of  $\text{Fe}_5\text{Zn}_{21}$ , that is, it has the same influence as other factors we have already discussed.

To answer this question, we carried out experiments in baths containing from 0.2 to 1% Al at temperatures from 450 to 600°C for periods of 30 sec to 10 min.

The results indicate that at 600°C the  $\text{Fe}_5\text{Zn}_{21}$  layer appears soon after immersion, even if the bath contains considerable amounts of aluminum.

To find a quantitative characteristic of the influence of aluminum on the formation of intermetallic layers, we determined the minimum immersion time which elapses before such layers start to form in all the alloys we studied. We call this time the incubation period, and Figure 48 shows the dependence of its duration (in minutes) on the content of aluminum in the bath at 450, 500, and 600°C.

From these curves the following conclusion can be drawn:

- 1) At a given temperature the incubation period increases with increase in the content of aluminum in the bath.
- 2) At a given aluminum content in the bath this period decreases with increase in the temperature of the bath. Thus, in baths containing 0.4% Al the intermetallic layers appear after 7 minutes at 450°C, after 5 minutes at 500°C, and after 3 min at 600°C.
- 3) For each temperature there is a maximum content of aluminum which must not be exceeded if the time for the formation of coatings should not be increased. This maximum is lower at higher temperatures of the bath.

These conclusions can be a starting point for determining the amount of aluminum that must be added to the bath.

It has been found that there is a quantitative difference between the formation of  $\text{Fe}_5\text{Zn}_{21}$  from baths with and without aluminum. In baths of pure zinc the  $\text{Fe}_5\text{Zn}_{21}$  compound is not formed immediately but after a certain period. The length of this period is influenced by various factors, including the temperature of the bath, the structure of the iron articles, and the content of aluminum in the liquid zinc bath.

Aluminum hinders the dissolution of iron in liquid zinc even more than the formation of  $\text{Fe}_5\text{Zn}_{21}$ . This has been confirmed, because coatings obtained from baths with up to 0.1% Al or more do not contain  $\text{FeZn}_7$  crystals or a  $(\text{FeZn}_7 + \text{Zn})$  eutectic which are signs of the dissolution of iron in liquid zinc.



## CONCLUSION

1. For a study of the reactive diffusion of metals the principle of this phenomenon must be understood. At the beginning of the second part of this book we found that there are differences of opinion on the fundamental principles of reactive diffusion. Today, no one doubts that diffusion can exceed the limits of metal solubility, that is intermetallic phases can be formed below the melting point of the reacting metal, but the conditions for such processes are still not clear. Some authors believe that the formation of intermetallic phases during diffusion is the result of the saturation of the solid (or liquid) solution of one metal by another.

This limitation appears unfounded, since we are convinced that the formation of new phases as a result of the interaction between two metals can take place irrespective of solubility. In the general case, reactive diffusion should be considered as a complex process of the formation of phases by a direct chemical reaction (reactive diffusion), or as the result of supersaturation of the solid solution. Accordingly, the reactions of solid metals with liquid, which we are mainly considering, can produce intermetallic compounds in two ways: as a result of an equilibrium (or diffusion) when the new phase is produced by supersaturation of the liquid solution with the high-melting metal; or as the result of a direct reaction in which the new phase is formed on the interface of the two reacting metals. There is no doubt that the first process occurs, and that the phase with the lowest melting point which is in a state of equilibrium with a liquid solution is produced at the beginning of the process.\*

For the second process by which new phases can be formed it is assumed that not only the phase with the lowest melting point is formed during the first moment of the reaction, but also other phases that may possibly be produced under the given conditions.

Therefore, during a study of reactive diffusion of metals, we were concerned chiefly with the physicochemical nature of the phases and the sequence of their formation.

A study of a number of metallic systems has shown that phases which are not in a state of equilibrium with the liquid solution can be formed at the beginning of the interaction between metals. This proves that reactive diffusion can produce intermetallic phases by a direct chemical reaction on the surface, irrespective of the conditions of dissolution. This was the first conclusion, and we believe a very important one, derived in the second part of the book.

\* It is assumed that this phase is formed during the interaction of the solid metal with a liquid. It is also possible that a new phase is formed only after the reaction has stopped, that is during the solidification and cooling of the liquid left on the surface of the high-melting metal. It is clear that this cannot be classified as reactive diffusion since only the saturation of the liquid alloys with the high-melting metal occurs during the reaction, or in other words this is a normal diffusion process.

Therefore, the interaction between two metals may be the result of: either a diffusion process leading to the formation of equilibrium phases which on the phase diagram border on the pure starting metals or their solid solutions; or a "reactive" process by which various phases are formed irrespective of the condition of the reaction.

2. The second part of this book (Chapters II and III) describes the kinetics of reactive diffusion.

We first studied the rates of diffusion within the intermetallic phases (growth rate). This problem is of practical importance, and it is also interesting since it shows the differences between diffusion in ordinary solid solutions ("atomic" diffusion) and in intermetallic phases.

This study has shown that diffusion within intermetallic phases occurs in the same way as in solid solutions with lattices of the basis metal. Under certain limiting conditions the growth of the diffusion layer is governed by a parabolic law ( $y^2 = 2pt$ ) where the parameter of the parabola ( $p$ ) is analogous to the diffusion coefficient and differs from it only by a constant factor.

To determine the diffusion coefficient from the parameter of the parabola, there is only the Frenkel—Sergeev formula /77/ which is rather approximate. From their experimental data on the parameter  $p$  for  $\text{Cu}_2\text{Zn}_5$  and  $\text{Fe}_5\text{Zn}_{21}$  phases, Frenkel and Sergeev calculated the following diffusion coefficients for  $400^\circ\text{C}$ :

$$\begin{aligned} \text{for } \text{Cu}_2\text{Zn}_5, \quad D &= 2 \cdot 10^{-3} \text{ cm}^2/\text{day} = 2 \cdot 10^{-8} \text{ cm}^2/\text{sec}, \\ \text{and for } \text{Fe}_5\text{Zn}_{21}, \quad D &= 2 \cdot 10^{-4} \text{ cm}^2/\text{day} = 2 \cdot 10^{-9} \text{ cm}^2/\text{sec}. \end{aligned}$$

Since we believe that as in the case of atomic diffusion the temperature dependence of the diffusion coefficient is the best characteristic of the intermetallic phases, we studied the dependence of the parameter  $p$  on temperature, and for a number of systems derived the following experimental equation:

$$p = Ae^{-Q/RT}$$

This result shows once again that diffusion processes occur in the lattices of solid solutions and of intermetallic compounds.

The value of  $Q$  corresponds to the heat of "loosening," both qualitatively and quantitatively, and therefore it is the most convenient characteristic for comparing diffusion rates in different phases.

This comparison showed that although for intermetallic phases the values of  $Q$  are on an average somewhat lower than for ordinary solid solutions, they are of the same order of magnitude. It was also found that, with a few exceptions, phases with a similar structure (according to the Hume-Rothery classification) formed in various metallic systems have very similar values of  $Q$ , and the small differences are explained well by the different melting points. Thus, here too, we have complete agreement with the solid solution.

It should be also pointed out that the experimental determination of the values of the diffusion coefficients (parameter  $p$ ) and of the heat of "loosening"  $Q$  for diffusion within intermetallic phases is very simple to carry out.

3. The rate of growth of intermetallic phases determines the kinetics of the diffusion in solids. However, if a solid reacts with a liquid, we must assume that several processes take place simultaneously. The two following are the most important: 1) dissolution of the high-melting metal in the liquid, and the formation (by diffusion) of equilibrium phases; 2) a chemical reaction on the interface leading to the formation of "reactive" phases. The kinetics of the action and the final structure of the diffusion layer are apparently determined by the rates of these two processes. This assumption was the basis for a wide study of the reactions between solid and liquid metals in the iron—zinc system.

In this research we used the ratio between the rates of dissolution and chemical reaction on the interface to explain the temperature curve of the reactions of iron with zinc (with a characteristic shape which has not yet been explained), and the structures formed by these processes. The theory we derived generalizes the process by which several different structures can be formed.

The influence of the structure of the basis metal can also be explained by the ratios between the rates of dissolution and chemical reaction. In the reaction between iron and zinc this influence determines not only the nature of the diffusion layer but also the kinetics of the process. This is of great practical importance and is discussed in this book.

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APPENDIX

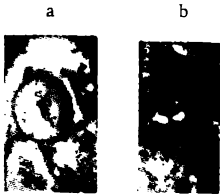


PLATE 1. Diffusion of Ag in Cd:

a — plane of basis; b — plane perpendicular to basis.

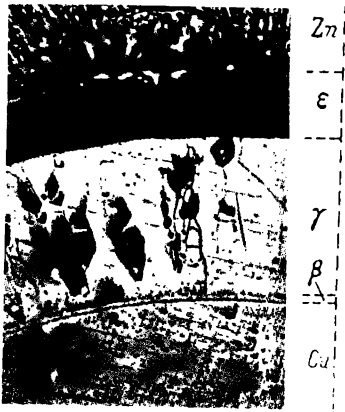


PLATE 2. Diffusion in Cu—Zn systems at 430°C for 7 hr.  $\times 100$ .

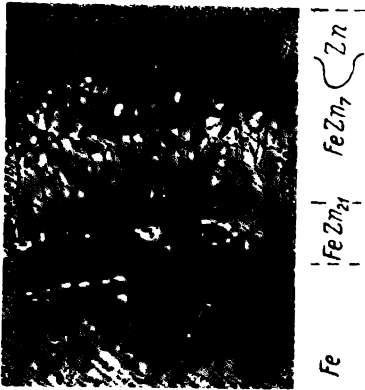


PLATE 3. Diffusion in Fe—Zn systems at 430°C for 3 hr.  $\times 100$ .



PLATE 4. Diffusion in Cu — Cd systems at 500°C for 15 min.  $\times 200$ .

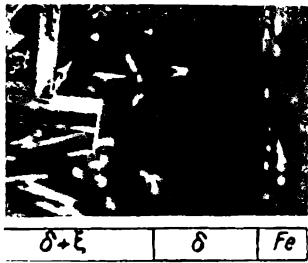


PLATE 5. Structure of zinc coating according to Scheil and Wüst

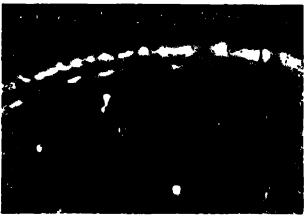


PLATE 6. Reaction of iron with zinc: 0.15 %C; 420°C.  $\times 100$ .

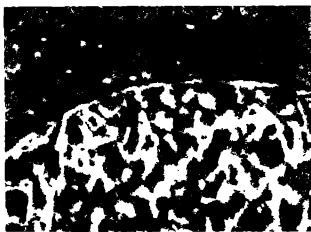


PLATE 7. Reaction of iron with zinc:  
0.5% C; 420°C.  $\times 100$ .



PLATE 8. Reaction of iron with zinc:  
0.5% C; 450°C; 1 min quenching in water.  $\times 250$ .



PLATE 9. Reaction of iron with zinc:  
0.5% C at 450°C; 3 min.  $\times 250$ .



PLATE 10. Reaction of iron with zinc:  
0.15% C at 450°C; 20 min.  $\times 250$ .



EXPLANATORY LIST OF USSR ABBREVIATIONS  
APPEARING IN THIS BOOK

Abbreviation	Full name (transliterated)	Translation
AN SSSR	Akademiya Nauk SSSR	Academy of Sciences of the USSR
GNGU	Gosudarstvennoe Nauchnoe Gidrograficheskoe Uprav- lenie	State Scientific Hydrographic Administration
GTTI	Gosudarstvennoe Izdatel'- stvo Tekhniko-Teoreti- cheskoi Literaturny	State Publishing House of Technical and Theoretical Literature
ONTI	Otdel Nauchno-Tekhn- cheskoi Informatsii	Department of Scientific and Technical Information
ZhETF	Zhurnal Eksperimental'- noi i Teoreticheskoi Fiziki	Journal of Experimental and Theoretical Physics
ZhTF	Zhurnal Tekhnicheskoi Fiziki	Journal of Technical Physics













